United States Court of Appeals

for the Second Circuit

APPENDIX

DEFERRED JOINT APPENDIX TO THE BRIEFS
Vol. 2 of 3
Pages 424 - 1190

74-1683

74-1687

IN THE
UNITED STATES COURT OF APPEALS
FOR THE SECOND CIRCUIT

No. 74-1683

HOOKER CHEMICALS AND PLASTICS CORPORATION, STAUFFER CHEMICAL COMPANY, AND MONSANTO COMPANY,

Petitioner,

v.

RUSSELL E. TRAIN,

Respondent.

No. 74-1687

HOOKER CHEMICALS AND PLASTICS CORPORATION, STAUFFER CHEMICAL COMPANY, AND MONSANTO COMPANY,

Petitioner,

v.

RUSSELL E. TRAIN,

Respondent.

On Petition For Review Of Action Of The
Administrator Of The Environmental Protection Agency

ROBERT C. BARNARD
DOUGLAS E. KLIEVER
HENRY J. PLOG, JR.

1250 Connecticut Avenue, NW
Washington, DC 20036

ATTORNEYS FOR PETITIONERS

Of Counsel:

CLEARY, GOTTLIEB, STEEN & HAMILTON
1250 Connecticut Avenue, NW
Washington, DC 20036
December 20, 1974

only copy available

PAGINATION AS IN ORIGINAL COPY

GENERAL

1. DO YOU FORESEE ANY CHANGES IN YOUR WASTE LOAD IN THE NEXT FEW YEARS (RAW MATERIAL OR PROCESS CHANGES, PRODUCT PURITY, ETC.) ?

2. CAN THE PRESENT MANUFACTURING PROCESS BE MODIFIED OR CHANGED TO SIGNIFICANTLY REDUCE EFFLUENT WASTE LOADS ?

3. DO "GOOD HOUSEKEEPING" PRACTICES HAVE A MAJOR BEARING ON YOUR EFFLUENT COMPOSITIONS OR ARE THEY COMPOSITIONS DETERMINED ENTIRELY BY BY-PRODUCTS OF THE PROCESS OR QUALITY OF RAW MATERIALS USED ?

YES

4. DOES THIS PLANT HAVE ANY UNIQUE WASTE SITUATIONS AS COMPARED TO OTHER PLANTS PRODUCING THE SAME CHEMICALS (RAW MATERIAL SUPPLY, PROCESS, GEOGRAPHICAL LOCATION, OTHER) ?

MORE COOLING WATER, FEWER LEAKS DUE TO PLANT CONSTRUCTION

5. ARE THE TREATMENT PROCESSES NOW USED-----

a. SENSITIVE TO SHOCK LOADS?

b. SHUTDOWN AND STARTUP ?

c. MAINTENANCE REQUIREMENTS ?

6. IS TECHNOLOGY AVAILABLE FOR ELIMINATION OF YOUR PLANT WASTE PROBLEMS ?

7. IF NOW AVAILABLE, WHAT DO YOU CONSIDER THESE TECHNOLOGIES TO BE ? (EVAPORATION, DISTILLATION, DEEP WELLS, AERATION PONDS, FILTRATION, NEUTRALIZATION, ETC.)

8. HOW DO YOU RATE THE COST OF UTILIZING THIS TECHNOLOGY IN SOLVING YOUR PLANT WASTE PROBLEMS ?

9. IF NOT AVAILABLE, WHAT TECHNOLOGY NEEDS TO BE DEVELOPED ?

10. IS ADDITIONAL RECYCLING OF EFFLUENT STREAMS PRACTICABLE ?

11. ARE RECOVERY AND SOLID WASTE ISOLATION TECHNIQUES PRACTICABLE, AND IF SO, WHERE ?

12. WILL THE INSTALLATION OF PROJECTED WASTE CONTROL FACILITIES CAUSE AIR, NOISE, THERMAL OR OTHER POLLUTION EFFECTS?

hooker Industrial chemicals DIVISION

COLUMBIA, TENNESSEE 38401, PHONE (615) 388-6752

April 24, 1973

Mr. Leon Parker
General Technologies Corporation
6621 Electronic Drive
Springfield, Virginia

Dear Mr. Parker:

The following costs pertain to water treatment and handling in Hooker's Columbia phosphorus plant.

Capital costs -- 689,000. This cost is for installations made from 1952 through 1972.

Operating costs -- 170,000 per year. This is based on current operation.

I hope this information will be of use.

Very truly yours,

HOOKER CHEMICAL CORPORATION

T. T. Garrett

T. T. Garrett
Plant Engineer

TTG/pr

GENERAL TECHNOLOGIES CORPORATION
INTER-OFFICE MEMORANDUM

Date: April 23, 1973
303-95

To : 303 Distribution

From : E. F. Abrams

Subject: Trip Report to Hooker Chemical Company's Phosphorus Chemical Plant in Columbus, Mississippi, on April 19, 1973.

I talked with the following people:

Irving Power, Plant Manager, Columbus;
Ray Crosby, Plant Engineer, Columbus;
Tyson Whittaker, Process Engineer, Columbus; and
J. B. Hufford, Production Superintendent, Columbus.

After speaking with Ed Smith and Ed Rissmann before this trip I was fully expecting to find at this plant the manufacture of four different phosphorous chemicals: P_2O_5, PCl_3, $POCl_3$ and P_2S_5. However, when I arrived at the plant I found out that they make only one of these chemicals P_2S_5, and their main product at the plant is sodium chlorate. I felt this slightly unusual, as a couple of days before I had spoken with Ed Smith who was up at Niagara, and asked Ed about the possibility of visiting their Niagara plant since they also make phosphorous chemicals. His answer was why visit the Niagara plant when they make the same chemicals at Columbus, and Columbus would be an easier plant to sample. This was brought to the attention of Irv. Power, who indicated that Ed Smith knows better but probably wasn't thinking at the time. Apparently Sargent will have to visit the Niagara plant after he comes on board for the rest of the phosphorous chemicals.

The waste products in this plant are phosphorous mud coming from the reactor seals, amounting to about a tenth of a pound per ton of product. This mud is collected and land-filled. Another waste is continuous boiler blow-down and wastes from the water treatment of their well water before going in to the boiler.

Future wastes will emanate from a recently installed scrubber on their casting operation to reduce the P_2O_5 formed during the casting operation, when the P_2S_5 burns at the surface while they're casting. The scrubber presently is using only water, which is not doing the job of absorbing the P_2O_5. They are considering using either a dilute solution of phosphoric acid to absorb

303 Distribution - 4/23/73

it, or possibly a caustic soda or lime water treatment in the scrubber. Presently there are no treatment facilities for the water-borne effluent, and all of the water that goes through the plant is discharged directly into the Tom Bigby River. After examining the process and plant, and water system, I was able to find a man hole where samples could be taken which emanate only from the P_2S_5 area of the plant. I informed the people there that we would possibly like to sample the plant with the crew presently in Texas. This would make the sampling visit about the 30th of April. It will be necessary to contact Mr. Power, the Plant Manager several days in advance, to make sure that the plant is in normal operating condition when the sampling crew gets there.

WATER INPUTS TO PLANT

TYPE	QUANTITY, GPD	COMMENTS ON SOLIDS, MINERALS, TREATMENTS, ETC.
RIVER		
LAKE		
MUNICIPAL		
WELL	72,000 MIN. 144,000 MAX.*	only boiler H2O is treated
OTHER		

WATER USAGE

TYPE	TOTAL QUANTITY, GPD	% RECYCLED
COOLING	BALANCE of + 17,000	17,000 Flaker cooling H2O
PROCESS		
OTHER Seal H2O	7500	
OTHER FUTURE SCRUBBER	3600	

COMMENTS

* Flaker cooling operates only about 2 times/week

PRESENT TREATMENT INFORMATION

	METHOD	WHEN INSTALLED	CAPITAL COSTS	OPERATING COSTS	STREAMS TREATED
1.					
2.	None for H2O effluent				
3.					

PERFORMANCE OF TREATMENT METHODS

	METHOD	QUALITATIVE RATING	WASTE REDUCTION* ACCOMPLISHED
1.			
2.		N/A	
3.			

*% REDUCTION IN WASTE LOAD AS MEASURED BY SUCH QUANTITIES AS TOTAL SUSPENDED OR DISSOLVED SOLIDS, CHLORIDES, SULFATES, pH, BOD, ORGANICS, ETC.

GENERAL TECHNOLOGIES CORPORATION
INTER-OFFICE MEMORANDUM

To : 303 Distribution

Date: 23 May 73

From : D. H. Sargent DH

Re: 303-120

Subject: Plant Visit - PCl_3, $POCl_3$
FMC, Nitro, W. Va. 5/21/73

The manufacture of PCl_3 is essentially by the standard process, except that the reaction is conducted semi-continuously instead of batch-wise. The manufacture of $POCl_3$ is by the air-oxidation of PCl_3 instead of the Standard process which utilizes P_2O_5 and Cl_2 to oxidize PCl_3 . At FMC, the product $POCl_3$ is filtered, with landfilling of used cartridge filter elements (after washing).

As in the Standard process (see 303-119), the sources of aqueous wastes include:

(1) Phossy water from transfer of liquid phosphorus.
(2) Water scrubbers on continuous process vent lines.
(3) Water scrubbers for fumes from product transferring operations and product holding tanks.
(4) Periodic cleanout of residues in semi-batch reaction vessels and still pots.
(5) Washing of returned shipping containers prior to reuse.
(6) Washing of used filter elements.

Several important steps have been incorporated in the FMC operation:

(1) When liquid phosphorus is transferred from a rail car to the plamt's storage tank, the phossy water displaced from the storage tank is pumped back into the emptying rail car. This phossy water is shipped back to the phosphorus-producing facility (for treatment and/or reuse) instead of being wasted at the PCl_3 plant. The only phossy water wastes are minor due to surges or to anomalies in the storage tank water level control system.

(2) Although returned product tank cars are water-washed at FMC, the returnable drums are cleaned by an off-site subcontractor, thereby reducing this plant's waste load.

(3) The product storage tanks are diked to contain any spillage or leaks from mechanical pump seals.

(4) The cooling water is recirculated through a cooling tower; only the blow down is discharged (into the Kanawha River).

(5) The arsenic-enrichened residue from the PCl_3 distillation is periodically cleaned out without release of arsenic. First, the residue is treated with trichloroethylene, in which PCl_3 is miscible but $AsCl_3$ is not. The trichloroethylene is then water-washed to remove the arsenic-free PCl_3 and the trichloroethylene is reused. The $AsCl_3$-rich fraction is then segregated and stored in drums; a means for final disposal is now under investigation.

At the present time, the aqueous wastes, containing phosphoric acid, phosphorus acid, and hydrochloric acid are discharged to the river. FMC is committed to the State, however, to install a lime-neutralization unit this year for the entire acidic wastes of the Nitro Plant (of which PCl_3 and $POCl_3$ wastes are a very small part). No provisions will be included for removal of suspended solids or of soluble phosphates or chlorides.

FMC CORPORATION

ORGANIC CHEMICALS DIVISION

BOX 547, NITRO, WEST VIRGINIA 25143 • TELEPHONE: (304) 755-3351

June 13, 1973

Dr. Leon Parker
General Technologies, Incorporated
6621 Electronic Drive
Springfield, Virginia 22151

Dear Dr. Parker:

On May 30, and 31, 1973, two representatives of General Technologies (Frank Bialas and Mike Calhoon) were at this plant to sample and analyze the normal effluents from the $PCl_3/POCl_3$ plant. I am sending to you, under separate cover, a sample of wash water from our tank car cleanouts which was not available when your analysts arrived at the plant.

The tank car cleanouts generate 4,000/8,000 gallon (6,000 gallon average) of wash water every three weeks.

When your analysis of the sample is complete, please send a copy of your results to my attention. If you have any questions concerning the sample, please do not hesitate to contact me.

Very truly yours,

FMC CORPORATION
Industrial Chemical Division

Roger Morrison

R. V. Morrison
Process Engineer

RVMorrison/et

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FMC, Nitro, W.Va Sample recieved 6/18
Sample: Tank car Cleanout water

ph: <4

~~ph~~

cond: 4900 mg/l NaCl;

Cl^-: ~~(1:40).53×50×40~~ : (1:10) 1.43 × 50 × 10 = 715

phos. (ortho) : 1:10 - ~2.1 ×10 = 21

1:40 - .52 ×40 = 20.8 - 21

phos. (total) 1:100 - .26 ×100 = 26

~~Ferrous Thiocyanate comparison~~
~~Stock solution 200 ppm~~ ~~Distilled Rhut~~
probably best to absorption ~~in glass~~ container

6000 gal in 3 wks = 2000 gal/wk = 286 $\frac{gal}{day}$

$\frac{286 \frac{gal}{day}}{115 \text{ tons/day}} = 2.49$ gal/ton

ANALYSIS FORM - HOME LAB

Plant FMC Date _____ Identifying No. _____

Location Nitro W. Va Sample Site Air Scrubber Stream

Product _____

Parameter	Number of Measurements	Individual Measurements	Average
Phosphorus (P_4)			
Heavy Metals: Mercury			
Lead			
Arsenic			
Vanadium			
Aluminum			
Titanium			
Iron			
Chromium			
Organics			
TDS	2	564, 570 ppm	567 ppm
SS	3	34, 30, 34 ppm	33 ppm

REMARKS: _____

SIGNATURE(S) _____

ANALYSIS FORM - HOME LAB

Plant FMC Date _____ Identifying No. X

Location Nitro W. Va Sample Site Truck Loading Scrubber

Product _____

Parameter	Number of Measurements	Individual Measurements	Average
Phosphorus (P_4)			
Heavy Metals: Mercury			
Lead			
Arsenic			
Vanadium			
Aluminum			
Titanium			
Iron			
Chromium			
Organics			
TDS	1	194 ppm	194 ppm
SS	1	0 ppm	0 ppm

REMARKS: _____

SIGNATURE(S) _____

4.9

ANALYSIS FORM - HOME LAB

Plant fmc
Location Nitro, W. Va
Product

Date
Sample Site fifth cleanout drum
Identifying No. 7

Parameter	Number of Measurements	Individual Measurements	Average
Phosphorus (P_4)			
Heavy Metals: Mercury			
Lead			
Arsenic			
Vanadium			
Aluminum			
Titanium			
Iron			
Chromium			
Organics			
TDS	1	9,700 ppm	9,700 ppm
SS	1	4 ppm	4 ppm

REMARKS:

SIGNATURE(S)

Note: Submission of Part A is required of all applicants whose processes are listed on page 3 above.)

(Office use only)

Discharge Serial No. 001

INFORMATION REQUIRED OF SPECIFIED INDUSTRIES

PARAMETER AND CODE	Intake: DAILY AVG. CONCENTRATION UNTREATED INTAKE WATER (1)	Intake: DAILY AVG. CONCENTRATION TREATED INTAKE WATER (2)	Discharge: MAXIMUM CONCENTRATION (3)	Discharge: MAXIMUM POUNDS PER DAY PER PROCESS UNIT (4)	Discharge: DAILY AVG. CONCENTRATION MAXIMUM POUNDS PER DAY (5)	Discharge: AVERAGE POUNDS PER DAY (6)	Discharge: SAMPLE TYPE (7)	Discharge: SAMPLE FREQUENCY (8)	Discharge: METHOD OF ANALYSIS (9)	Discharge: CONTINUOUS MONITORING (10)	(11)
~~ALKALINITY (as $CaCO_3$)~~ Acidity 00410 00435	5	-	1,556	*	58,038	925	33,275	CONT	DYLY	STD, MTHDS 12th Ed p, 46	ABS
B.O.D. 5-DAY 00310	3	-	165	*	6,765	80	2,875	CONT	DYLY	" " p,415	ABS
CHEMICAL OXYGEN DEMAND (C.O.D.) 00340	* 14	-	2,271	*	81,634	297	10,674	CONT	DYLY	" p,410	ABS
TOTAL SOLIDS 00500	270	-	1,233	*	47,705	906	33,337	CONT	DYLY	" p,244	ABS
TOTAL DISSOLVED SOLIDS 70300	231	-	1,170	*	42,248	826	30,536	CONT	DYLY	" p,245	ABS
TOTAL SUSPENDED SOLIDS 00530	39	-	408	*	15,708	80	2,801	CONT	DYLY	" p,246	ABS
TOTAL VOLATILE SOLIDS 00505	* 33.3	-	*	*	*	87.3	3,139	CONT	* OTHR	FWPCA pp,261 -267	ABS
AMMONIA (as N) 00610	* 0.5	-	*	*	*	0.5	17.98	CONT	* "	FWPCA pp,127 -142	ABS
KJELDAHL NITROGEN 00625	* 1.83	-	*	*	*	1.74	62.56	CONT	* "	FWPCA pp,145 -159	ABS
NITRATE (as N) 00620	* 0.68	-	*	*	*	0.24	8.63	CONT	* "	FWPCA pp,165 -170	ABS
PHOSPHORUS TOTAL (as P) 00665	* 0.30	-	*	*	*	14.91	536.07	CONT	* "	FWPCA pp,222 -232	ABS

ENG FORM 4345-1 MAY 71

* See Remarks.

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FMC/Nitro

FMC/Nitro

J. Davis
Shaw

$POCl_3$ Plant Sewer H_2O

Orig: Sargent

Date	$CaCO_3$ Acidity (ppm)	Cl^- (ppm)	pH
	1	5	1
2/27/73	1170	560	2.1
2/28/73	1220	603	2.1
3/1/73	1720	822	1.8
4/19/73	850	447	2.3
4/23/73	480	305	2.3
4/24/73	950	532	2.0
4/25/73	1430	851	2.0
4/26/73	1250	589	1.9
4/27/73	1300	1035	1.7
4/30/73	1120	518	2.0
5/1/73	1470	1040	1.8
5/2/73	1690	716	1.8
5/3/73	280	773	2.6
5/4/73	1340	603	1.9
5/7/73	1810	1000	1.7
5/8/73	1220	574	2.2
5/9/73	1290	716	2.2
	20610	11684	34.4
	avg 1213	687	2.02

Roger Morrison

Some data. Aren't we getting a lot of samples

Norm.

5-9-73

flow - maybe 20 GPM. Measure

ANALYSIS FORM

Plant FMC
Location Nitro, W. Va.
Product PCl_3; $POCl_3$

Date 5/30/73
Identifying No. 1
Sample Site ~~Stream~~ Air Scrubber Stream

Parameter	Number of Measurements	Individual Measurements	Average
Flow *		30 GPM	
Temperature		21 - 23 °C	
Color APHA-std.		80	
Turbidity FTU		25	
Conductivity mg/l NaCl		1800	
Suspended Solids		20	
pH		2.0 - meter ; <4 - Hach kit	
Acidity: Total		500	
Free		370	
Alkalinity (Total) P/T			
Hardness: Total		81	
Calcium		61	
Halogens: Chlorine			
Chloride		450	
Fluoride			
Sulfate		35	
Phosphates (Total) inorg. as PO_4		65 ; ortho - 63	
Nitrogen (~~Total~~) NO_3, as N		.36	
Heavy Metals: Iron		12	
Chromate			
Hydrogen Sulfide			
Oxygen (Dissolved)			
BOD			
COD			

REMARKS: * flow from line computed from operational water usage figures of the 3 scrubbers, supplied by R. Morrison.

SIGNATURE(S) D. A. Bialas ; Michael Callahan

ANALYSIS FORM

Plant FMC
Location Nitro, W. Va.
Product PCl_3, $POCl_3$

Date 5/30/73
Sample Site City Water

Identifying No. 2

Parameter	Number of Measurements	Individual Measurements	Average
Flow		—	
Temperature		—	
Color		-0-	
Turbidity		-0-	
Conductivity mg/l NaCl		77	
Suspended Solids		-0-	
pH		7.15	
Acidity: Total		—	
Free		—	
Alkalinity (Total) P/T		-0-/36	
Hardness: Total		65	
Calcium		59	
Halogens: Chlorine			
Chloride		18	
Fluoride			
Sulfate		24	
Phosphates (~~Total~~) ortho as $PO_4^{\equiv}$		.18	
Nitrogen (~~Total~~) NH_3 as N		.15	
Heavy Metals: Iron		.03	
Chromate			
Hydrogen Sulfide			
Oxygen (Dissolved)			
BOD			
COD			

REMARKS:

SIGNATURE(S) T. O. Bialas, Michael Calhoun

ANALYSIS FORM

Plant fmc Date 5/30/73 Identifying No. 7

Location Nitro, W. Va. *Sample Site filter Cleanout Drum

Product PCl_3; $POCl_3$

Parameter	Number of Measurements	Individual Measurements	Average
Flow *		5.5 Gal/day	
Temperature			
Color		0	
Turbidity		0	
Conductivity mg/l NaCl		52,000	
Suspended Solids		10	
pH		<4 - hach kit ; .5 - meter	
Acidity: Total		18,200	
Free		13,100	
Alkalinity (Total) $\frac{P}{T}$		—	
Hardness: Total		—	
Calcium		—	
Halogens:			
Chlorine			
Chloride		6500	
Fluoride			
Sulfate		27	
Phosphates (Total) inorg. as $PO_4^{\equiv}$		590 ; ortho - 400	
Nitrogen (~~Total~~) NO_3 as N		0	
Heavy Metals:			
Iron		420	
Chromate			
Hydrogen Sulfide			
Oxygen (Dissolved)			
BOD			
COD			

REMARKS: *Samples (and discharge volumes) collected by fmc personnel; ~~at~~ at request of EPC (Don Sargent).

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SIGNATURE(S) F. O. Bialas / Michael Calhoun

ANALYSIS FORM

Plant FMC Date 5/30/73 Identifying No. X

Location Nitro; W. Va. *Sample Site Truck Loading Scrubber

Product PCl_3; $POCl_3$

Parameter	Number of Measurements	Individual Measurements	Average
Flow *		240 Gal/day	
Temperature		—	
Color		0	
Turbidity		0	
Conductivity		1800	
Suspended Solids		0	
pH		24 - hach kit ;	
Acidity: Total		660	
Free		450	
Alkalinity (Total) P / T		—	
Hardness: Total		—	
Calcium		—	
Halogens:			
Chlorine			
Chloride		340	
Fluoride			
Sulfate		29	
Phosphates (Total) inorg. as $PO_4^{\equiv}$		260 ; ortho - 220	
Nitrogen (~~Total~~) NO_3 as N		.47	
Heavy Metals:			
Iron		.09	
Chromate			
Hydrogen Sulfide			
Oxygen (Dissolved)			
BOD			
COD			

REMARKS: * See sample 7

SIGNATURE(S) T. A. Bialas ; Marshall Colburn

GENERAL TECHNOLOGIES CORPORATION
INTER-OFFICE MEMORANDUM

To : 303 Distribution

Date: 4 Jun 73

From : D. H. Sargent DS

Re: 303-124

Subject: Plant Visit – Calcium Phosphates
Occidental Chemical, Davenport, Iowa, 5/30/73

This plant manufactures calcium phosphates for livestock feed, as opposed to the food-grade product reported previously (303-121). Although both types are made by neutralizing phosphoric acid with lime and by drying the resulting salt, the non-food-grade production is different in a number of important respects:

(1) Lower-quality wet-process phosphoric acid is used for livestock feed manufacture as opposed to food-grade furnace acid. A preliminary process step is the defluorination of much of the wet-process acid, resulting in large quantities of scrubber water waste heavy in fluorides.

(2) A minimum of process water is used, since the market is tolerant to significant quantities of monocalcium phosphate (MCP) in the dicalcium phosphate (DCP) product. For food-grade DCP manufacture, excess process water is necessary to ensure reaction homogeneity. Hence, there is no raw waste load from a dewatering unit operation as there is in the food-grade process.

(3) Because there is only one product and because the purity requirements are minimal, the scrubber water effluents from wet dust collectors and various dry solid raw wastes may be directly returned to the process. Such is not the case for food-grade calcium phosphate plants.

At the exemplary Occidental Davenport plant, three separate water cycles are used and there is no effluent from any. The acid defluorination scrubber water is neutralized with lime, the solids are settled by ponding, and the pond effluent is reused as scrubber water. The scrubber water for collection of air-borne solids from the reactor and dryer is recirculated with a bleed-off directly into the reactor as process water. Cooling water is recycled through a cooling tower, with the blowdown used as makeup in the solids scrubbing system instead of being wasted. Softened well water is used for cooling water makeup.

The only wastes from this plant are the effluent from regeneration of the water softener and some runoff when rain washes solids from exterior plant surfaces.

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Suppl B
PHOSPHATE
7

Monsanto

Monsanto Company
5045 W. Jefferson Avenue
Trenton, Michigan 48183
Phone: (313) 676-4400

PH05

April 23, 1973

Mr. Lee C. McCandless, Manager
Special Coatings Department
General Technologies Corporation
6621 Electronic Drive
Springfield, VA 22151

Dear Mr. McCandless:

During your visit to Monsanto's Trenton, Michigan Plant, April 5, 1973, I gave you a comprehensive book of data which included:

1. History of the Trenton Plant, including product information.

2. A location map, including cross section of the two outfalls.

3. A block diagram depicting river water distribution. The river water is used as once through cooling water. City water and steam distribution is essentially the same.

4. A block diagram of our lime/phosphate precipitation process.

5. All non-confidential data supplied the Corp of Engineers for discharge permits, both outfalls. i.e., Parts A and B.

6. The complete field and laboratory report by EPA, Region V, Michigan District Office, March, 1972, (73B), covering a 24 hour sampling of both outfalls.

In addition, we toured the Lime/Phosphate Precipitation Plant and looked at sampling points your field crew could use.

You asked for additional data as follows:

Attachment A - A water balance across the entire plant.

Attachment B - Sampling points and average flow while operating.

Attachment C - The amount of process water and percent which is recycled.

Attachment D - The raw waste load to the Lime/Phosphate Precipitation Plant including phosphate, sodium, suspended solids, and dissolved solids.

Attachment E - Tons of filter cake/day hauled from the lime/phosphate precipitation process to land fill.

Attachment F - A block flow diagram of the (STP) sodium tripolyphosphate process.

Attachment G - Pounds phosphate lost to the Detroit River per ton of phosphorus utilized.

Attachment H - The Treatment Plant operating and capital costs, including components of the abatement program such as sewer separations.

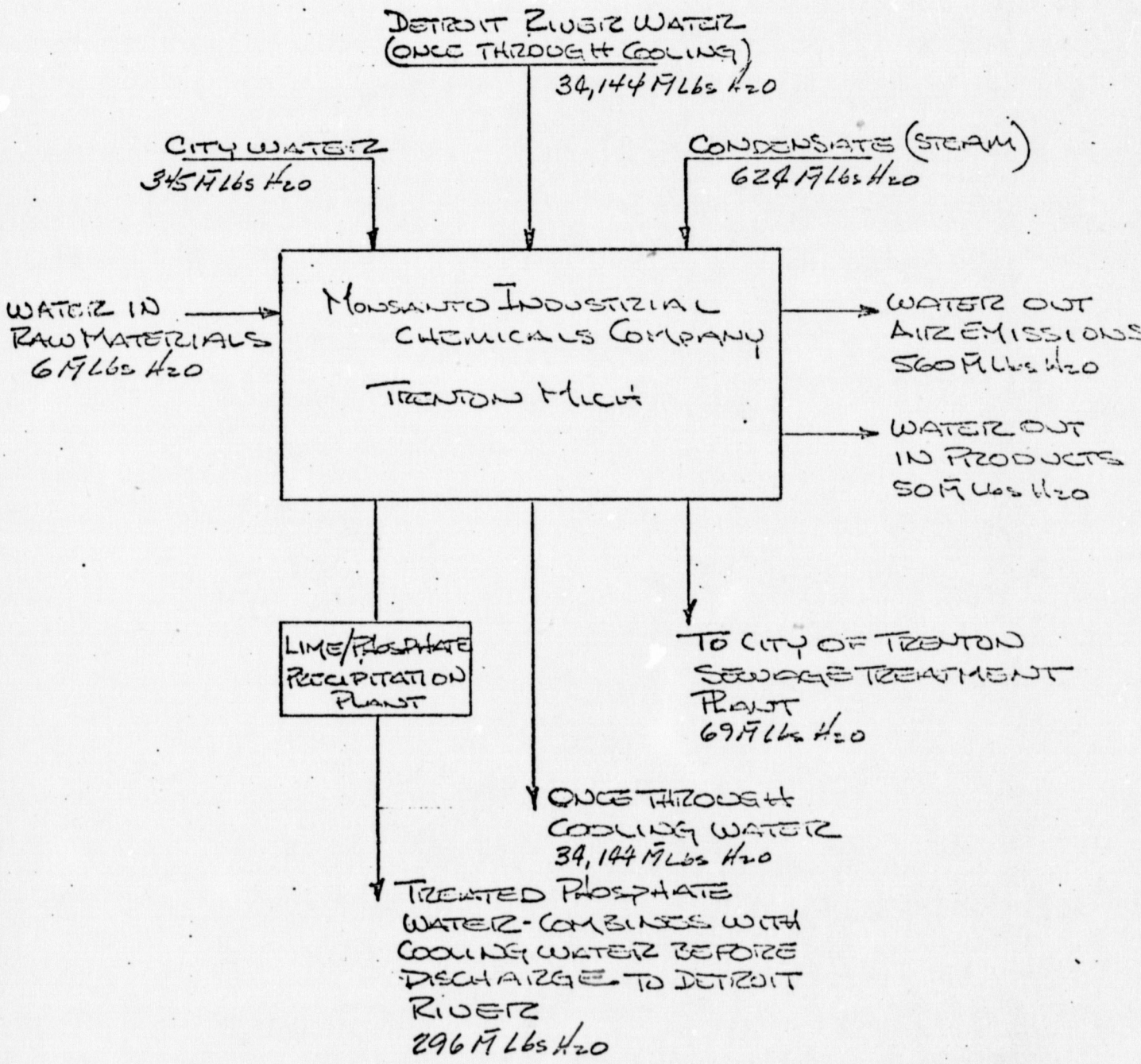
If I can be of further service, please advise.

Very truly yours,

Bryan J. Sevey

attach.
idb

MICC
TRENTON, MICHIGAN
WATER BALANCE - BASE, YEAR 1972
(EXPRESSED AS MILLIONS OF POUNDS H_2O)

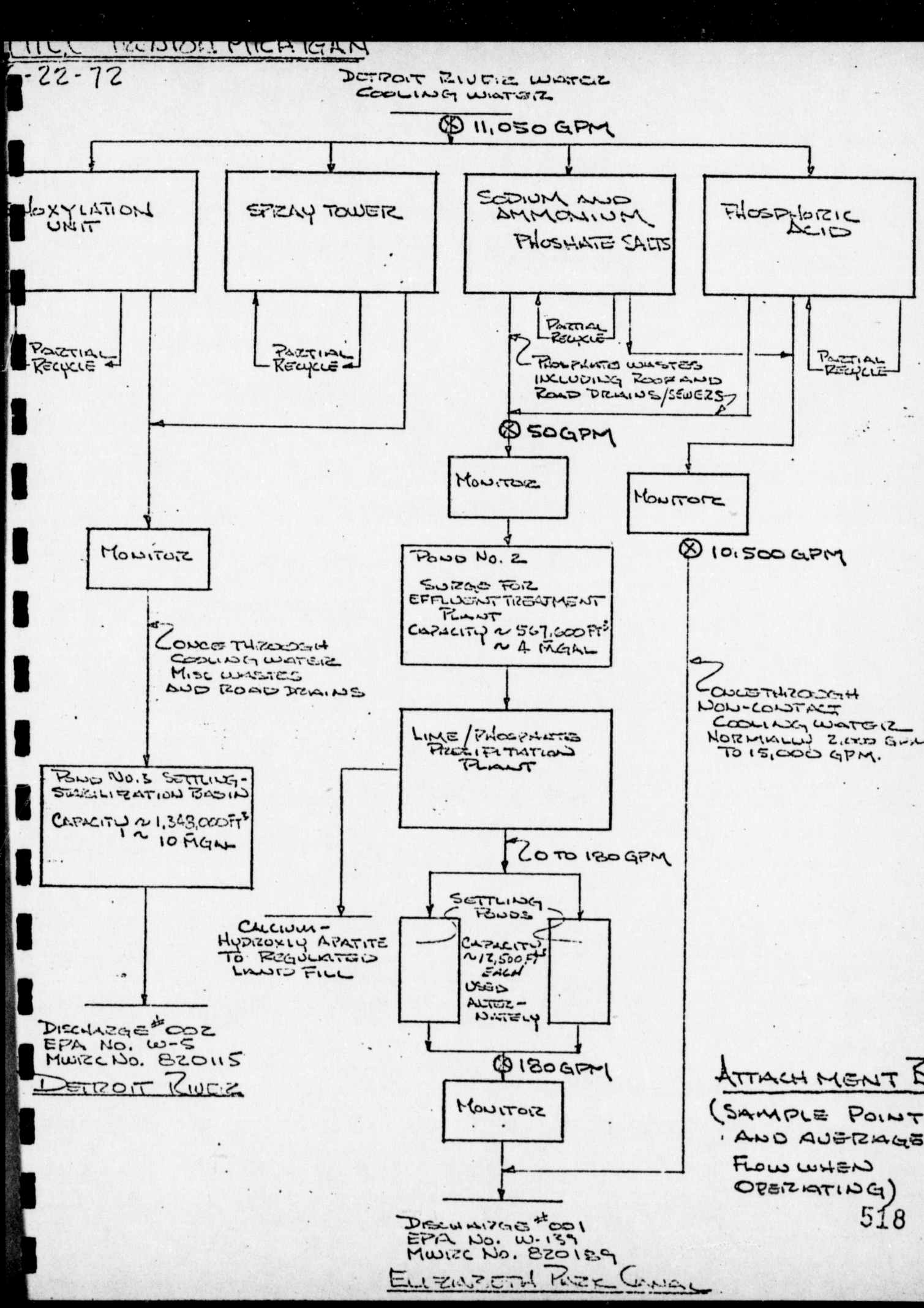


ATTACHMENT A

RLS 4-18-73

MCC TRENTON, MICHIGAN

7-22-72



ATTACHMENT N

(SAMPLE POINTS AND AVERAGE FLOW WHEN OPERATING)

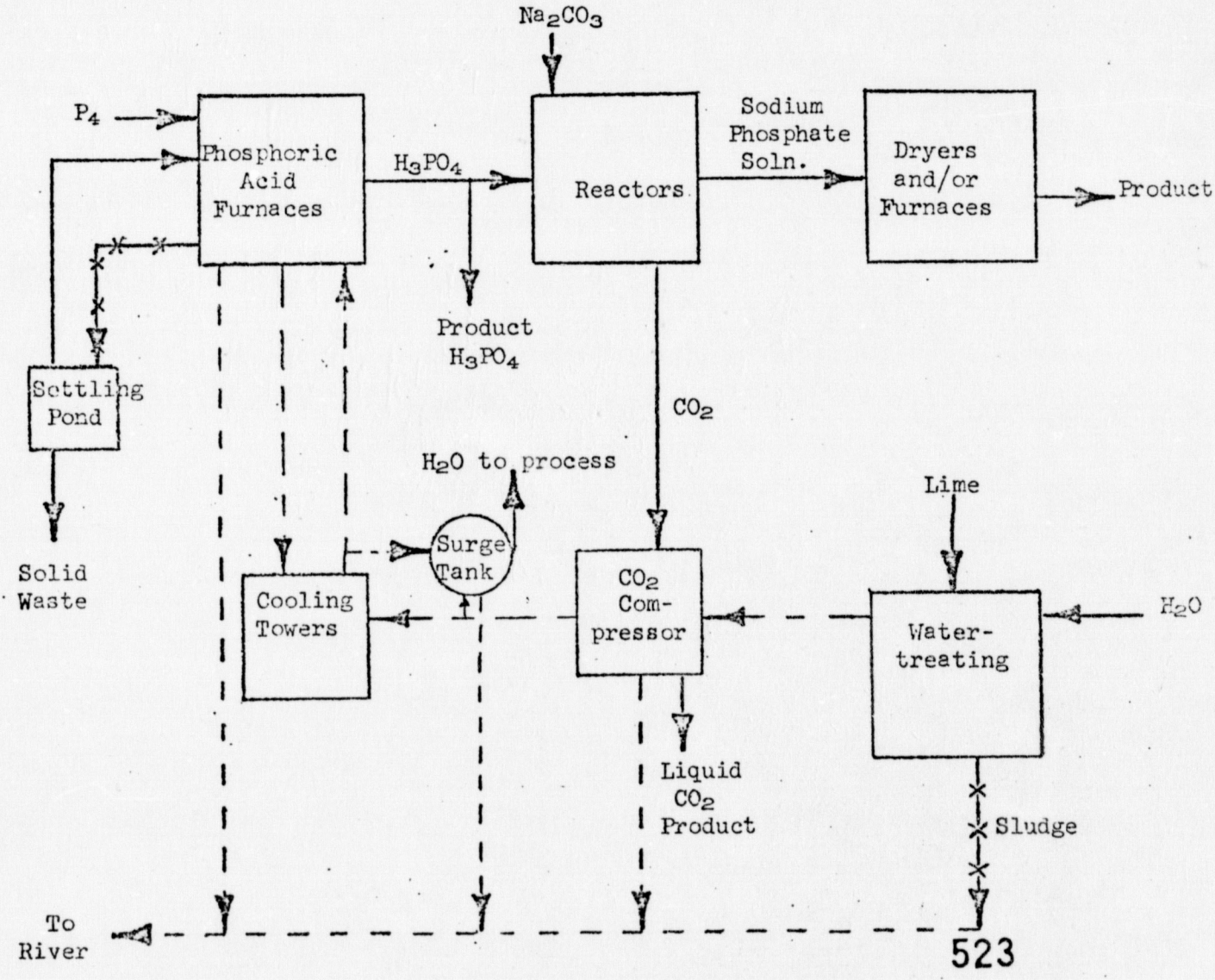
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PLANT WASTE ANALYSIS

COMPANY FMC Corporation
PLANT LOCATION Lawrence, Kansas
PRODUCT(S) Sodium Phosphates, Phosphoric Acid
IS THIS A STANDARD PROCESS FACILITY?

PLANT AGE 22 yrs
TONS/DAY ~ 200 as P_4
DATE March 27, 1973
YES X NO

PROCESS FLOW DIAGRAM (SCHEMATIC)
(Please include location of waste streams)



Process streams
Water
Area drainage
Waste stream

CONFIDENTIAL PENDING DETERMINATION

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RAW MATERIALS FOR PRODUCT

MATERIALS	ORIGIN AND PURITY COMMENTS
1. Elemental phosphorus	Idaho ore As_2O_3 - ~ 200 ppm
2. Soda ash	Wyoming trona
3. Caustic soda	Wichita, Ks
4.	
5.	

STANDARD RAW WASTE LOADS

WASTE PRODUCTS	PROCESS SOURCE	LBS/TON OF PRODUCTS					
		OPERATION		STARTUP		SHUTDOWN	
		AVE.	RANGE	AVE.	RANGE	AVE.	RANGE
1.							
2.							
3.							
4.							
5.							
6.							

COMMENTS

Waste products as such are not generated by our processes. The presence of objectionable constituents in our effluent is due entirely to water softening process and contamination due to spillage.

Confidential Information - Trade Secrets

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CONFIDENTIAL PENDING DETERMINATION

GENERAL TECHNOLOGIES CORPORATION
INTER-OFFICE MEMORANDUM

Date: 23 May 73

To : 303 Distribution

Re: 303-121

From : D. H. Sargent DS

Subject: Plant Visit - Calcium Phosphates
Monsanto, Carondelet (St. Louis), Mo. 5/18/73

In the standard process for manufacturing calcium phosphates, food-grade phosphoric acid is neutralized with lime slurry in batch tanks. The amount of process water used, the lime-to-phosphoric acid ratio, and the degree of solid product drying are tailored to make either MCP, monocalcium phosphate (anhydrous or monohydrate); DCP, dicalcium phosphate dihydrate; or TCP, tricalcium phosphate. Process water is introduced both in the lime slurrying operation and into the neutralization reaction tanks. The resulting MCP slurry is spray-dried, the DCP slurry is first centrifuged and then kiln-dried, and the TCP slurry is drum-dried (steam-heated drums).

The raw aqueous wastes from the plant are from two sources: the centrate from the DCP separation and the effluent from wet scrubbers (for the MCP spray dryer vent and for the DCP kiln vent). Both of these sources contain significant quantities of suspended, finely divided calcium phosphate solids. The scrubber water is partially recycled to reduce the hydraulic waste quantity.

The combined centrate and scrubber effluent is treated with lime to maximize precipitation of any residual phosphate ion, and thengravity-thickened. The thickener overflow, containing lime and some calcium phosphate suspended solids and having a very high pH, is the plant effluent. The thickener underflow is recycled back to the process after a proprietary unit operation.

The thickener overflow, however, is not discharged directly to a receiving stream but is sent via the sanitary sewer to the St. Louis Metropolitan Sewer District Treatment Plant. Monsanto must control pH to a maximum of 10.5, and pays a user charge based not only on hydraulic load but upon suspended solids. This SS surcharge is $27 per ton over and above 350 ppm.

CONFIDENTIAL PENDING DETERMINATION

Monsanto is in the process of replacing the wet scrubbers with baghouses. This change is being economically justified on the basis of usable product recovery, but it will have the side virtue of reducing the plant raw waste load to DCP centrate only.

One fundamental constraint exists in improving the performance of the gravity thickener. Polymeric flocculents could significantly reduce the suspended solids in the effluent, but they cannot be used here since the product is all food grade and they would contaminate recycle streams.

Cooling water for the exothermic reactions is completely segregated from process water, and is separately discharged (without recycle) into the adjacent River Das Perez. Combined with this cooling water discharge is storm water; this is a possible source of contaminated discharge since all exterior surfaces of the plant are coated with fine lime and/or calcium phosphate dusts.

CONFIDENTIAL PENDING DETERMINATION

Date 5/25/73 Identifying No. 1

[redacted] Location St. Louis, Mo. (Carondelet) Sample Site Drum Tank overflow

[redacted] Product: Di-calcium phosphate

[redacted] Parameter	Number of Measurements	Individual Measurements	Average
[redacted] Flow		range (0-150 GPM ; ave. - 52 GPM	
[redacted] Temperature °C		36°C	
Color (APHA-Std)		>500	
[redacted] Turbidity (Formazin = JTU)		550	
Conductivity mg/l as NaCl		3900	
[redacted] Suspended Solids mg/l		>500	
pH		9.9	
[redacted] Acidity: Total mg/l as $CaCO_3$		—	
Free		—	
[redacted] Alkalinity (Total) P / M		400 / 2,400	
[redacted] Hardness: Total		6	
Calcium	↓	-0-	
[redacted] Halogens: Chlorine			
[redacted] Chloride mg/l as Cl^-		5	
Fluoride			
[redacted] Sulfate mg/l as $SO_4^=$		-0-	
[redacted] Phosphates (Total) Inorganic mg/l as PO_4		21,000 ; ortho - 3400	
Nitrogen (Total) NOT mg/l N		2.7	
[redacted] Heavy Metals: Iron mg/l		-0-	
[redacted] Chromate			
~~Hydrogen Sulfide~~			
~~Oxygen (Dissolved)~~			
~~BOD~~			
~~COD~~			

REMARKS:

544

[redacted] SIGNATURE(S) A.O. Bodas / Thabal Collins

[redacted] CONFIDENTIAL PERIOD DETERMINATION

MONSANTO INDUSTRIAL CHEMICALS COMPANY

CARONDELET PLANT

ST. LOUIS, MISSOURI

GENERAL TECHNOLOGIES CORP. VISIT

C. E. Powell
May 14, 1973

MONSANTO INDUSTRIAL CHEMICALS COMPANY

CARONDELET PLANT

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CONFIDENTIAL PENDING DETERMINATION

Discharge Serial No. 002

INFORMATION REQUESTED OF SPECIFIED INDUSTRIES

Intake | Discharge

PARAMETER AND BASIS	(1) DAILY AVG. CONCENTRATION UNTREATED INTAKE WATER	(2) DAILY AVG. CONCENTRATION TREATED INTAKE WATER	(3) MAXIMUM CONCENTRATION	(4) MAXIMUM POUNDS PER PROCESS UNIT	(5) MAXIMUM POUNDS PER DAY	(6) DAILY AVG. CONCENTRATION	(7) AVERAGE POUNDS PER DAY	(8) SAMPLE TYPE	(9) SAMPLE FREQUENCY	(10) METHOD OF ANALYSIS	(11) CONTINUOUS MONITORING
ALKALINITY (as $CaCO_3$)			55	1229	7077	927	4409	COMP	DYLY	STD. METH.	ABS
5-DAY			0	13	75	7	33	COMP	DYLY	STD. METH.	ABS
CHEMICAL OXYGEN DEMAND (C.O.D.)			0	56	322	36	171	COMP	DYLY	STD. METH.	ABS
TOTAL SOLIDS			278	4036	23240	3542	16848	COMP	DYLY	STD. METH.	ABS
TOTAL DISSOLVED SOLIDS			278	2240	12898	1951	9380	COMP	DYLY	STD. METH.	ABS
TOTAL SUSPENDED SOLIDS			0	1780	10249	1222	5812	COMP	DYLY	STD. METH.	ABS
TOTAL VOLATILE SOLIDS			0	264	1520	260	1237	COMP	DYLY	STD. METH.	ABS
AMMONIA (as N)			0.50	2.00	12	1.27	6	COMP	DYLY	STD. METH.	ABS
KJEDAHL NITROGEN			0.50	2.30	13	2.30	11	COMP	DYLY	STD. METH.	ABS
NITRATE (as N)			0.77	1.00	6	0.66	3	COMP	DYLY	STD. METH.	ABS
PHOSPHORUS TOTAL (as P)			0.02	921	5303	730	3472	COMP	DYLY	STD. METH.	ABS

CONFIDENTIAL PENDING DETERMINATION

Discharge Serial No.
002

CHEMICAL PARAMETERS OF INTAKE WATER AND DISCHARGE (See Table B-2)

PARAMETER AND CODE	Intake: UNTREATED INTAKE WATER (1)	Intake: TREATED INTAKE WATER (2)	Discharge: MAXIMUM CONCENTRATION (3)	Discharge: MAXIMUM POUNDS PER DAY PER PROCESS UNIT (4)	Discharge: MAXIMUM POUNDS PER DAY (5)	Discharge: DAILY AVG. CONCENTRATION (6)	Discharge: AVERAGE POUNDS PER DAY (7)	SAMPLE TYPE (8)	SAMPLE FREQUENCY (9)	METHOD OF ANALYSIS (10)	CONTINUOUS MONITORING (11)
ALKALINITY (as $CaCO_3$) [illegible]											
TOTAL ORGANIC [illegible] (T.O.C.) [illegible]		0	64.0		369	33.5	159	C	D	S	A
TOTAL HARDNESS [illegible]											
NITRITE (as N) [illegible]											
ORGANIC NITROGEN [illegible]											
PHOSPHORUS-ORTHO [illegible]											
SULFATE [illegible]		39.9	110		633	93	442	C	D	S	A
SULFIDE [illegible]		0	<0.05		0	<0.05	0	C	D	S	A
SULFITE [illegible]											
SURFACTANTS [illegible]											

EPA Form 7500-1 (7-71)

CONFIDENTIAL PERMITS DETERMINATION

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Discharge Serial No.
002

(cont.) CHEMICAL PARAMETERS OF INTAKE WATER AND DISCHARGE (See Table B-2)

PARAMETER NAME/CODE	UNTREATED INTAKE WATER (1)	TREATED INTAKE WATER (2)	MAXIMUM CONCENTRATION (3)	MAXIMUM POUNDS PER DAY PER PROCESS UNIT (4)	MAXIMUM POUNDS PER DAY (5)	DAILY AVG. CONCENTRATION (6)	AVERAGE POUNDS PER DAY (7)	SAMPLE TYPE (8)	SAMPLE FREQUENCY (9)	METHOD OF ANALYSIS (10)	CONTINUOUS MONITORING (11)
[illegible]RIDE		26	142		818	86.3	410	C	D	S	A
[illegible]IDE		0.00	<0.01		0	<0.01	0	C	D	S	A
[illegible]RIDE		0.94	0.46		3	0.40	2	C	D	S	A
[illegible]UM-TOTAL		.55	9500		55	7450	35	C	D	S	A
[illegible]NY-TOTAL											
[illegible]D-TOTAL		<10	<20		0	<20	0	C	D	S	A
[illegible]-TOTAL											
[illegible]UM-TOTAL											
[illegible]TOTAL											
[illegible]TOTAL		<1	20		0	15	0	C	D	S	A

[illegible]-1 (7-71)

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CONFIDENTIAL PUBLIC DETERMINATION

Discharge Serial No. 002

B-2. (cont.) CHEMICAL PARAMETERS OF INTAKE WATER AND DISCHARGE (See Table B-2)

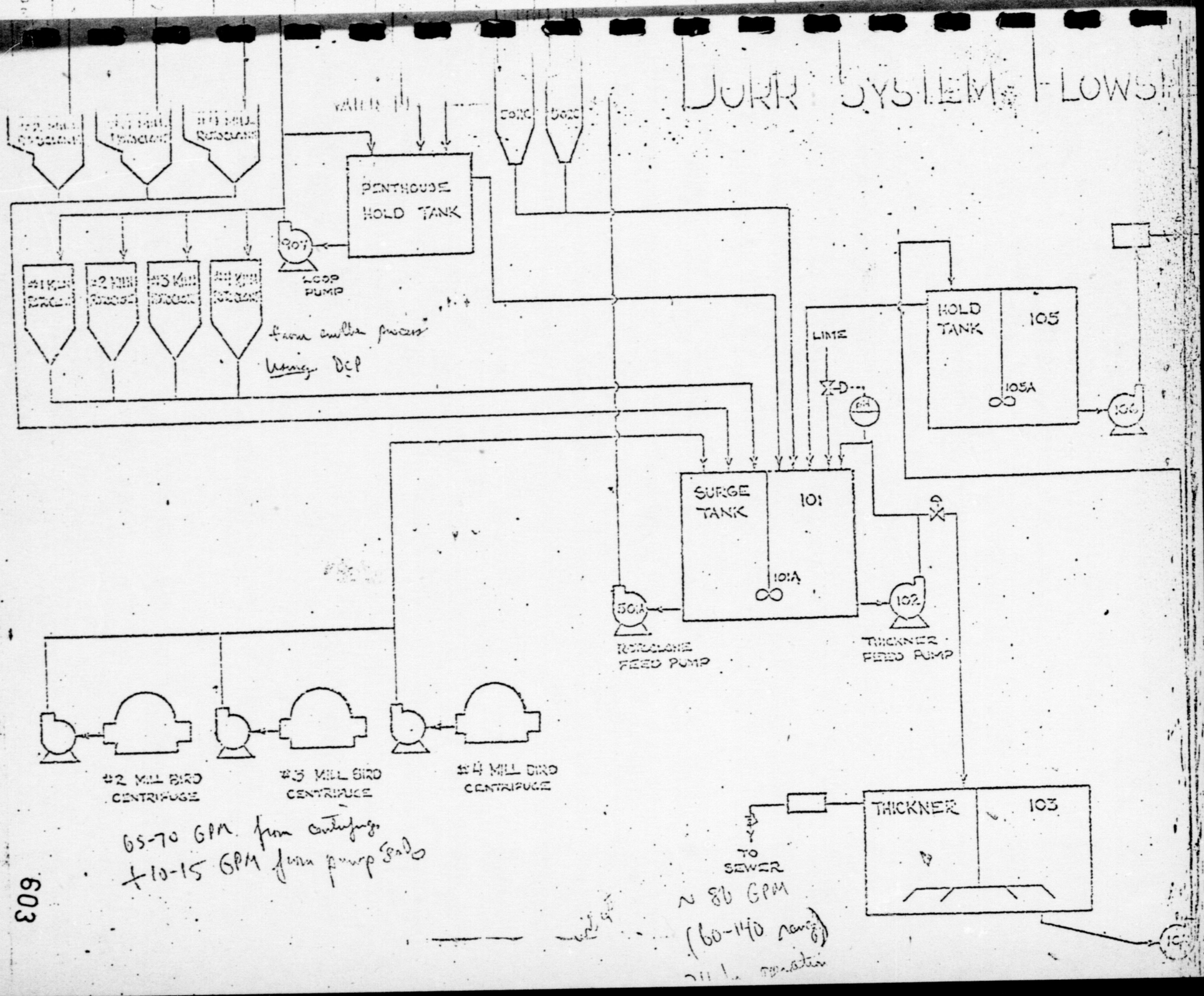
Intake		Discharge									
PARAMETER AND CODE	(1) UNTREATED INTAKE WATER	(2) TREATED INTAKE WATER	(3) MAXIMUM CONCENTRATION	(4) MAXIMUM POUNDS PER PROCESS UNIT	(5) MAXIMUM POUNDS PER DAY	(6) DAILY AVG. CONCENTRATION	(7) AVERAGE POUNDS PER DAY	(8) SAMPLE TYPE	(9) METHOD OF ANALYSIS	(10) CONTINUOUS MONITORING SAMPLE FREQUENCY
CALCIUM-TOTAL 00916		24.6	275		1583	263	1251	C	D	S
CHROMIUM-TOTAL 01034		<6	160		<1	145	<1	C	D	S
COBALT-TOTAL 01037										
COPPER-TOTAL 01042										
IRON-TOTAL 01045		64	3150		18	2625	12	C	D	S
LEAD-TOTAL 01051		4	120		<1	110	<1	C	D	S
MAGNESIUM-TOTAL 00927										
MANGANESE-TOTAL 01055										
MERCURY-TOTAL 71900		<0.1	<0.5		0	<0.5	0	C	D	S
MOLYBDENUM-TOTAL 01062										

Form 7560-1 (7-71)

CONFIDENTIAL PENDING DETERMINATION

Page 4

DURR SYSTEM FLOWS



603

GENERAL TECHNOLOGIES CORPORATION
INTER-OFFICE MEMORANDUM

Date: April 16, 1973

To : 303 Distribution

Re: 303-74
303-123

From : L. C. McCandless

Subject: Plant Visit - Monsanto Co, Soda Springs, Idaho
Elemental Phosphorus Plant

This plant is located in a very arid climate with a supply of high grade phosphate ore close by. The ore is not washed to remove impurities.

The phosphorus is produced by reacting blends of ore, sand and limestone in a nodulizer and then the nodules are fed to electrolytic furnaces. Ferro-phosphorus is produced as a by-product from the furnace.

Wastes from the process include:

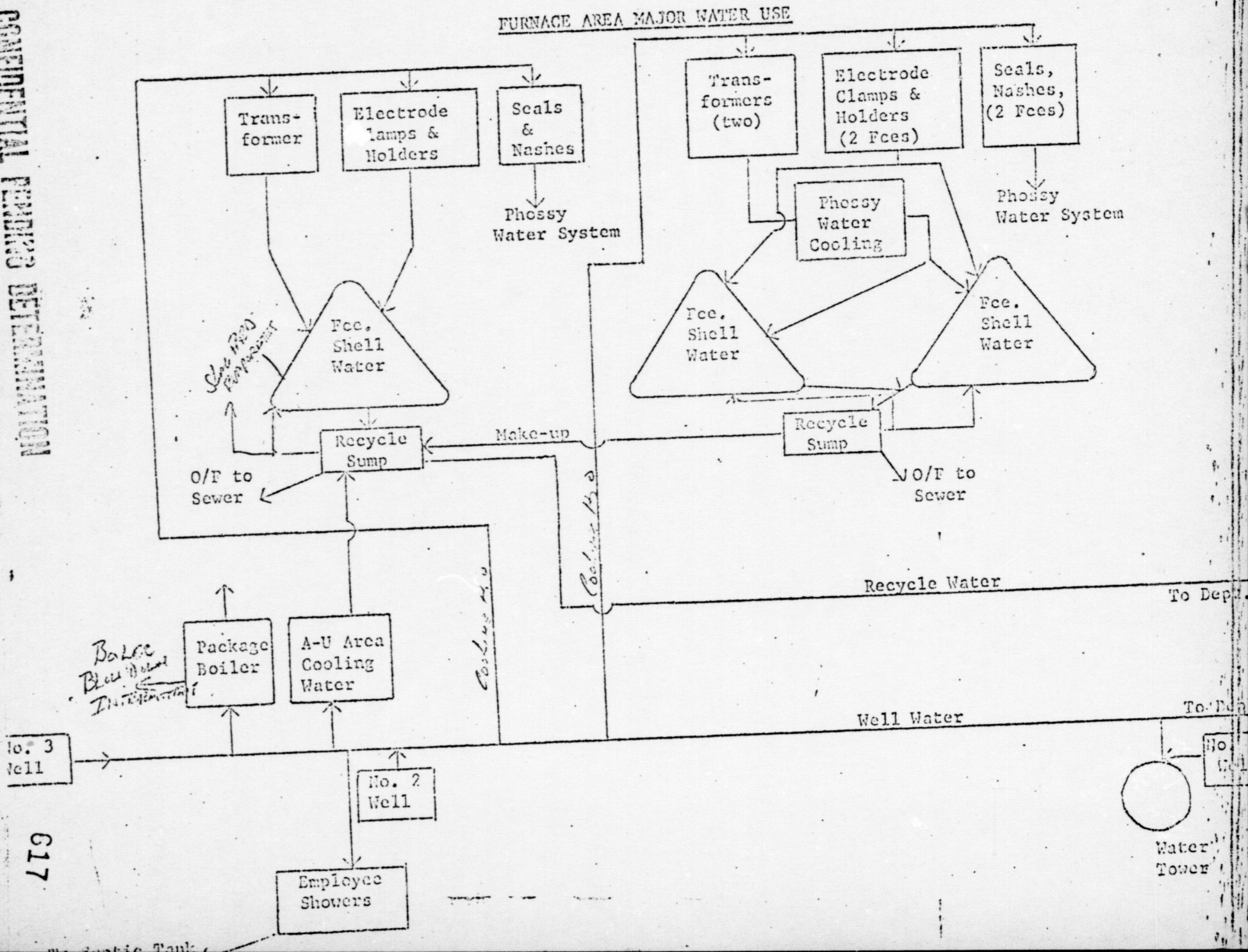
(1) Fluorine from the nodulizer
(2) Phosphorus particles from the electrostatic precipitator
(3) Miscellaneous phossy water from the process

The fluorine is scrubber from the nodulizer with lime solution and the waste is sent to a series of settling ponds. These ponds also receive cooling water and the pond overflows to the river. The phosphorus mud from the precipitator is dumped in an on-site landfill. The phossy water is collected and sent to a series of evaporation ponds with no discharge.

The plant bring in well water and discharges to a river. It must meet local water quality standards.

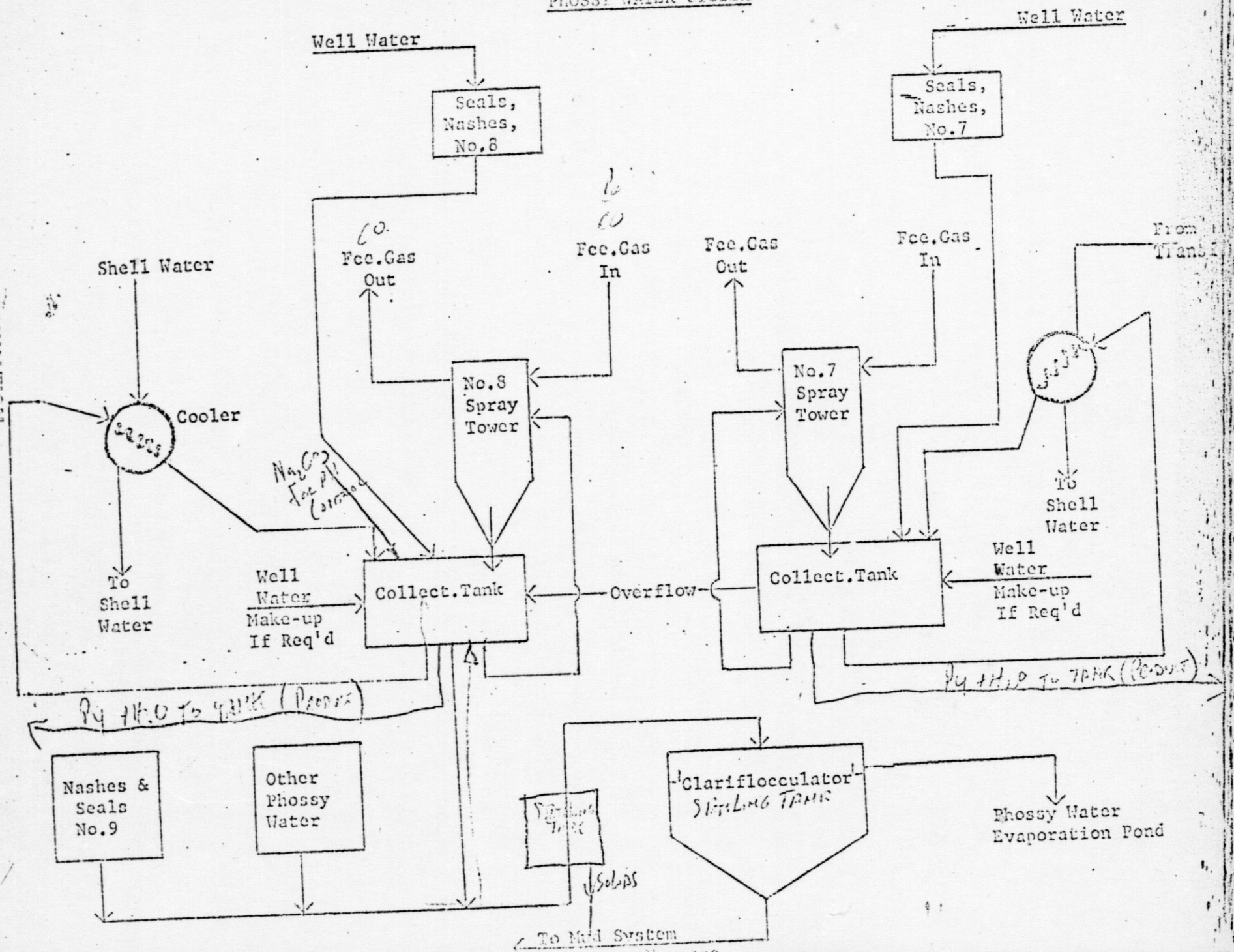
CONFIDENTIAL CONTAINS CLASSIFIED INFORMATION

FURNACE AREA MAJOR WATER USE



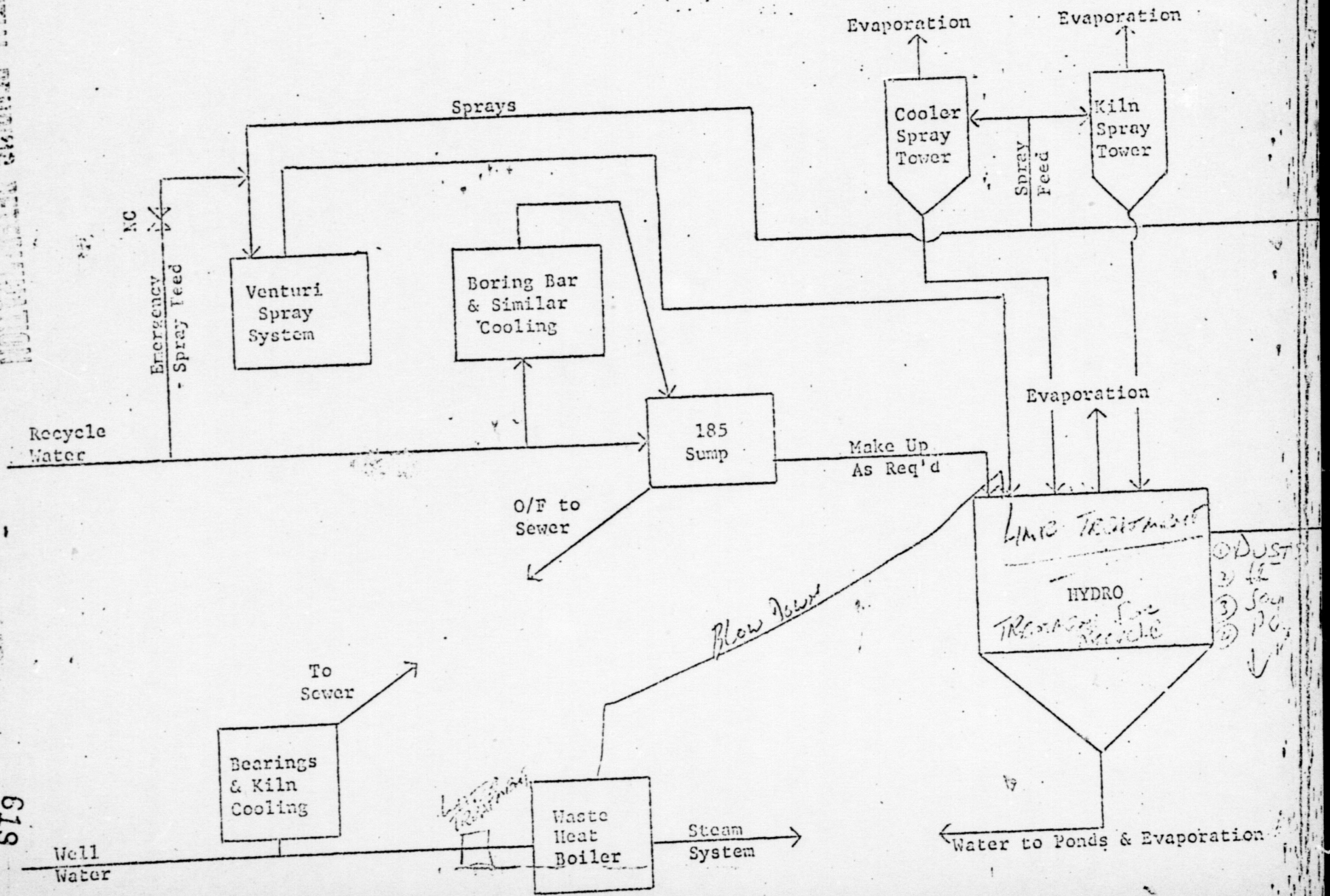
CONFIDENTIAL PENDING DECLASSIFICATION

PHOSSY WATER SYSTEM



DOCUMENTED GENERAL PUBLISHING

DEPT. NO. 10
MAJOR WATER USE



METHOD	WHEN INSTALLED	CAPITAL COSTS	OPERATING COSTS	STREAMS TREATED
1. Settling Pond	1952	Cost of this present installation is not significant. The circular pond is approximately 200 feet in diameter and 20 feet deep. Removing settled solids, the majority of which is from ground surface runoff, is done at 3 or 4 year intervals if necessary.		
2.				
3.				

PERFORMANCE OF TREATMENT METHODS

METHOD	QUALITATIVE RATING	WASTE REDUCTION* ACCOMPLISHED
1. Settling	Very Good	93 - 97
2.		
3.		

*% REDUCTION IN WASTE LOAD AS MEASURED BY SUCH QUANTITIES AS TOTAL SUSPENDED OR DISSOLVED SOLIDS, CHLORIDES, SULFATES, pH, BOD, ORGANICS, ETC.

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1. DO YOU FORESEE ANY CHANGES IN YOUR WASTE LOAD IN THE NEXT FEW YEARS (RAW MATERIAL OR PROCESS CHANGES, PRODUCT PURITY, ETC.) ?

NONE

2. CAN THE PRESENT MANUFACTURING PROCESS BE MODIFIED OR CHANGED TO SIGNIFICANTLY REDUCE EFFLUENT WASTE LOADS ?

Uncertain. Technology has not been developed for western phosphorus plants for total water recycle.

3. DO "GOOD HOUSEKEEPING" PRACTICES HAVE A MAJOR BEARING ON YOUR EFFLUENT COMPOSITIONS OR ARE THEY COMPOSITIONS DETERMINED ENTIRELY BY BY-PRODUCTS OF THE PROCESS OR QUALITY OF RAW MATERIALS USED ?

Phosphorus contaminated water must be contained, which involves good housekeeping and maintenance practices.

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PLANTS PRODUCING THE SAME CHEMICALS (WATER, MATERIAL SUPPLY, GEOGRAPHICAL LOCATION, OTHER) ?

Yes. Plant must operate in the winter with ambient temperatures to 40° F below zero. Recycle and cooling water streams would be expensive. Technology has not been developed to operate under severe winter conditions.

5. ARE THE TREATMENT PROCESSES NOW USED------ Not Applicable

a. SENSITIVE TO SHOCK LOADS?

b. SHUTDOWN AND STARTUP ?

c. MAINTENANCE REQUIREMENTS ?

6. IS TECHNOLOGY AVAILABLE FOR ELIMINATION OF YOUR PLANT WASTE PROBLEMS ?

Questions 6 through 12 deal with the technology a plant might use for control of waste problems. We feel we are using the best practical methods for treatment so these questions are combined and hopefully answered in the following chart. This chart is prepared to show different systems, treatment where applicable, amounts of collected materials and water usage.

CONFIDENTIAL FEDERAL DETERMINATION

Yes.

14. IF YOU WERE BUILDING A NEW PLANT COULD WASTE EFFLUENTS BE SIGNIFICANTLY REDUCED OR ELIMINATED ?

Not certain in the western climate.

15. MAY WE HAVE PERMISSION TO MAKE SPOT CHECK VERIFICATION MEASUREMENTS ON YOUR WASTE AND EFFLUENTS ?

Yes

16. IF SO PLEASE GIVE US:

NAME TO CONTACT P. Warner

APPOINTMENT DATE(S) _____

SAMPLE LOCATIONS (NEED PLANT LAYOUT WITH MARKED SAMPLING LOCATIONS)

CONFIDENTIAL PENDING DETERMINATION

WATER POLLUTION CONTROL

COLUMBIA ELEMENTAL PHOSPHORUS PLANT

J. G. DePAGTER

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CONFIDENTIAL PENDING DETERMINATION

MONSANTO INDUSTRIAL CHEMICALS COMPANY

COLUMBIA, TENNESSEE

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CONFIDENTIAL PENDING DETERMINATION

MONSANTO

Monsanto Company
Columbia, Tennessee 38401
Phone: (615) 388-3431

ITEM 21

DESCRIBE WASTE TREATMENT PRACTICES

Water enters the plant primarily from the Duck River with a small amount of process water arriving as ballast in railroad tank cars. The plant has two completely closed circuits, one for process water and one utilizing a cooling tower for cooling water from the furnaces. The process circuit recycles water from a settling pond to process spray towers to act both as an absorbant for fluorine and as coolant for off-gases from the kilns. This pond also receives elemental phosphorus contaminated water from our Furnace Department. Water evaporated in cooling the nodulizing kiln off-gases is in excess of the amount of phosphorus contaminated water, thus the closed loop on contaminated water works well in practice. No portion of either of these cycles is admitted to either No. 13 settling basin or the Duck River.

Three catch sump systems are located, one in the Furnace Department and two in the Nodulizing Department, to catch any leakage or emergency spills from the two circuits. Leakage or spills collected in these two catch sump systems are pumped automatically to the closed loop No. 3 pond system for disposal. In addition to the phosphorus contaminated water catch sumps, there is an emergency catch sump for collecting and handling any lime slurry leakage or spills from the lime slurry system that's used for neutralizing the fluorine absorbed by scrubbing kiln off-gases.

The No. 13 settling basin acts to remove particulate matter from all cooling and process water streams entering it. Cooling water from the Furnace Department and the Nodulizing Department enters No. 13 pond directly while process waters have the following pre-treatment:

1) Dust Collector Waters - Water from Furnace and Screening Plant Dust Collectors pass through a 24' hydro separator to remove solids before being released to No. 13 settling basin. Water from the Coke Plant Dust Collector passes through two preliminary settling basins before being released to the No. 13 settling basin.

2) Washer spillage passes through two settling basins before being released to the No. 13 settling basin.

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CONFIDENTIAL PENDING DETERMINATION

Monsanto Company
Columbia, Tennessee 38401
Phone: (615) 388-3431

ITEM 21 (Cont'd)
Page #2

3) Washer process water is part of a partially closed circuit. A portion of the washer process water passes through No. 15 tailings pond before being released to the Duck River through the No. 15 tailings pond siphon (outfall 003).

Another portion passes through No. 15 tailings pond, and No. 8 clear water pond and No. 2 tailings pond before being released to Duck River (outfall 002). This water enters No. 2 pond by seepage through a dike between No. 2 and No. 8 ponds.

A final portion of washer process water enters No. 13 settling basin after passing through No. 15 tailings pond and No. 8 clear water pond.

The balance of the washer process water is recycled directly to the Washer with make-up being taken from No. 13 settling basin. Surplus water from the No. 13 settling basin enters the Duck River (outfall 001).

We have continuous water monitoring stations on the Duck River above the plant intake, an outfall 001 from No. 13 settling basin, and on the Duck River below the plant at Hughes Bridge. For these points, turbidity, pH, temperature, and dissolved oxygen are recorded continuously. Also on these points, a continuous bioassy test using live native fish is maintained.

We also monitor the 002 outlet and the 003 outlet on a daily basis.

ITEM 22 (Cont'd)

Effluent description #2 tailings pond outfall. Serial #002. Receiving stream or point of discharge of storm sewer. Duck River. Stream mile 122. Latitude 35° 40' 00" Longitude 87° 07' 02".

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CONFIDENTIAL PENDING DETERMINATION

Monsanto Company
Columbia, Tennessee 38401
Phone: (615) 388-3431

ITEM 23 (cont'd)

Effluent description #15 tailings pond outfall. Serial 003
Receiving stream or point of discharge Duck River.

Stream Mile 121
Latitude 35° 40' 00" Longitude 87° 07' 02"

CONFIDENTIAL PENDING DETERMINATION

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GENERAL TECHNOLOGIES CORPORATION
INTER-OFFICE MEMORANDUM

Date: 18 Apr 73

To : 303 Distribution

Re: 303-81

From : L. C. McCandless

Subject: Plant Visit
Monsanto Phosphates - Trenton, Mich. 48183
5045 W. Jefferson - (313) 676-4400

Contacts: Mort Mullins - St. Louis
Chuck Malloch - Tech. Services Supt.
Bryan J. Sevey - Eng. Supervisor (Treatment Specialist)

This plant produces food grade and multiproduct phosphates. A good treatment for the SRWL from the complex is a lime precipitation, hydroclaifier, vacuum drying and solid disposal.

Monsanto recommends the following waste treatment for STP manufacture:

(a) minimize losses via good housekeeping and maintenance, maximize internal recycle and minimize water use. (Cooling water segregation is a must.);

(b) provide phosphate removal with public treatment facilities where possible;

(c) lime precipitation use should be minimized because of solid wastes generated, TDS "trade off" and pH high effluent.

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CONFIDENTIAL PENDING DETERMINATION

MONSANTO INDUSTRIAL CHEMICALS COMPANY
TRENTON, MICHIGAN

SUMMARY

GTC EFFLUENT GUIDELINE STUDY VISIT

April 5, 1973

1. Food grade and/or multi-product phosphate salts plant cannot, using available technology, achieve total recycle.

2. Of our four other STP manufacturing locations, three are essentially detergent grade STP only; the fourth, like the Trenton Plant, is both food grade and multi-product (i.e., sodium/calcium and potassium phosphates).

3. All utilize maximum internal recycle, and water conservation to minimize their discharges (to public treatment systems). We are engaged in a project at one of the STP plants to approach total recycle. We cannot yet claim that this ability is demonstrated.

4. We contend that the most practical waste treatment philosophy for STP manufacture is to:

   a. Minimize losses via good housekeeping and maintenance practices, maximum internal recycle and minimum water use.

   b. In those areas where phosphate limited eutrophication is a problem, provide phosphate removal at the public treatment level.

   c. Only in situations where unique political/economic considerations dictate, should lime precipitation be utilized. The solid wastes generated, the dissolved solids "trade off", and pH considerations are such that this process is less than a panacea, and across-the-board utilization would not be desirable.

CONFIDENTIAL PENDING DETERMIN

SOLUBLE PHOSPHATE RECOVERY

AT

MONSANTO'S TRENTON, MICHIGAN PLANT

BY

BRYAN J. SEVEY, ROBERT B. HUDSON, RONALD A. CAPELL, AND ROGER A. ROSE

PRESENTED AT THE

42ND ANNUAL CONFERENCE

OF THE

WATER POLLUTION CONTROL FEDERATION

DALLAS, TEXAS

OCTOBER 6, 1969

The floc is pumped to experimental dewatering ponds by means of a low-efficiency liquid-vortex type pump resulting in little floc degradation. The ponds allow the floc to settle out and the clear supernate overflows into a collection trough and monitor station, and is discharged into a phosphate-free cooling water sewer before entering a canal which discharges into the Detroit River. The ponds are ringed with 6 in. diam (15.24 cm diam) test wells to monitor any possible migration of high pH supernate. As a pond fills with solids it is removed from service, drained, mined, and the solids hauled to landfill operations approved by the Michigan Water Resources Commission and the appropriate County Health Department.

PROCESS OPERATIONS

The effluent treatment plant was operated intermittently for experimental purposes over a four (4) month period. Normal feed rate was 150 gpm (9.5 l/sec) with 75 gpm (4.7 l/sec) divided between the lime slaker and the primary reactor, with the other 75 gpm (4.7 l/sec) going to the secondary reactor. The phosphate concentration of the treatment plant feed was initially 1000 mg/l as P but gradually increased to 2500 mg/l. The low phosphate values and the gradual increase was due to partial evacuation of the feed pond during construction of the feed sump, and to stratification of the plant effluent mentioned earlier. A mixer has since been installed at the storage pond inlet which will help stabilize the phosphate concentration in the pond.

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The initial feed concentrations were below design and Ca/P ratios were as high as 5/1. Under these conditions the 24 hour settled effluent was crystal clear and contained less than 0.5 mg/l of total phosphorus. Subsequent operation at Ca/P ratios of 2/1 and 3/1 produced decanted effluents of 5 to 15 mg/l total

CONFIDENTIAL PENDING DETERMINATION

phosphorus. Filtered effluents however were almost invariable less than 0.5 mg/l indicating that some particulate material would not settle in 24 hours.

At one time, the plant was operated for two weeks with low-quality quicklime that resulted in Ca/P ratios less than 2. Under these conditions, the precipitate did not flocculate well, effluents were turbid and total phosphate in the supernatant solution on 24-hour settled samples averaged 360 mg/l. Phosphate removal averaged 85.5% even under these adverse conditions.

Settling pond effluent volume and phosphate concentration was monitored during all operations of the effluent treatment plant. Daily total P loss in the effluent averaged 63.3 lb/day (28.7 kg/day) over 60 full days of operation that included the operating period using low-quality quicklime. The low value was 1.35 lb (0.6 kg) and the high value was 460 lb (209 kg) during this period. The average loss was less than 10% of the allowable loss of 652 lb/day (296 kg/day) and did not exceed the allowable maximum during any 24-hour period.

The pH of the treated water is normally over 12. This effluent is mixed with 15,000 gpm (946 l/sec) of P-free cooling water that has sufficient buffering capacity to reduce pH of the combined flow to 9.5. The combined stream flows into a canal, shared with the adjacent power plant carrying several million gallons per minute for further dilution before discharge into the Detroit River.

PRESENT ACTIVITIES

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The process is now being modified as shown in Figure 3. Previously, the treated water was pumped to experimental dewatering ponds. However, the ponds failed to meet long-term objectives on effluent clarity and drying rate.

CONFIDENTIAL PENDING DETERMINATION

GENERAL TECHNOLOGIES CORPORATION
INTER-OFFICE MEMORANDUM

Date: March 1, 1973

To : 303 Distribution

303-41

From : R. G. Shaver

Subject: Trip Report - 2/28/73

Company: Monsanto Industrial Chemicals Co.
800 N. Lindbergh Blvd.
St. Louis, Mo. 63166

M. L. Mullins (Mort), Manager, Envir. Protection & Utilities
Howard C. Stanley, Attorney
James E. Feltham, Manager, Mfg. Technology, Phosphorus Dept.
Robert B. Hudson, Manager, Mfg. Technology (Phosphates)
(name unknown), Envirochem

1. Secrecy Agreement. A secrecy agreement format was given to me for our approval. A different one for every chemical product we study will be necessary. I will contact Stanley, the Attorney, about this in the next few days. This should not hold up plant visits.

2. Phosphorus. Feltham is the responsible person for this, but use Mullins for all contacts. It will take him one month to get his presentation prepared. We should arrange for phosphorus plant visits sometime after April 1, therefore. They strongly urged us to visit both the Columbia, Tenn. and the Soda Springs, Idaho plants, which are quite different. They said there are three different categories of P. plants: those in Florida, those in Tennessee, and the western plants. Water use rates and ore impurity contents differ greatly among these types. They also urge us to study the Hooper plant at Columbia, Tenn. as a total recycle plant.

3. STP. The sodium trysolyphosphate plant at Trenton, Mich. has its effluent going to a common treatment for all the many phosphate product effluents from this diverse facility (it makes all sorts of phosphates). However, they urge us to study it as an excellent end treatment process.

4. Sulfuric Acid. They have 4 plants, one a reclaim and 3 sulfur-burning. The one at Everett, Mass. is the newest - 3 years old, but all are single absorption plants and do not conform to new source air emission standards. The reclaim plant is next to a refinery and gives its wastes back to the refinery for treatment. It is probably of no use to us for this reason.

CONFIDENTIAL PENDING DETERMINATION

The Envirochem man gave us the following information on sulfuric acid:

(a) All built or under-construction plants meeting the new source requirements are now double-catalysis.

(b) There are several other processes that can also meet this requirement: the Purisieve process (molecular sieve, no water effluents), AMSOX ammonia scrubbing (possible water effluent and by-product sale), the CALSOX lime scrubbing (throw away lime sulfate and sulfite, the Anaconda smelter at Butte is considering this), and the Wellman-Lord sulfite solution scrubber.

(c) The wastes from sulfuric acid even on total recycle are as follows:

intermittent discharges of cooling water blow-down, waste heat boiler blow-down, and pump seal leaks and washes.

(d) In making oleum there is an additional brink scrubber.

5. Contacts. All technical contacts should be to Mort Mullins.

CONFIDENTIAL PENDING DETERMINATION

August 31, 1973

Subject: Action Memorandum on Proposed Effluent Limitations Guidelines, Standards of Performance, Pretreatment Standards for New Sources and Information on Alternative Treatment Methods for the Phosphorus Derived Chemicals Segment of the Phosphate Manufacturing Point Source Category.

From: Effluent Standards and Water Quality Information Advisory Committee

Dr. Robert B. Grieves

Dr. Martha Sager, Chairman

To: Acting Administrator, U.S.E.P.A.

The guideline of zero discharge of elemental phosphorus for Level I technology from all segments of the industry is BPT and is achieved today by virtually all plants in the industry.

The guideline of zero discharge of PO_4-P, F, and TSS (total suspended solids) for the three broad industrial segments is not BPT and it should not be the Level I guideline. The recommendation of zero discharge is based on two plants: Hooker Chemical and TVA's Muscle Shoals Plant. However, General Technologies Corporation did not visit TVA's plant, based its decision on two, open literature references, and misinterpreted those references: in fact, TVA's Muscle Shoals Plant does not achieve zero discharge. To establish BPT on the basis of one plant (Hooker) is not reasonable.

Instead of zero discharge, the following range of values is recommended as Level I technology:

PO_4-P: 0.2-0.4 lb/ton

F : 0.2-0.3 lb/ton

T.S.S: 0.5-1.0 lb/ton

Within the indicated range, the exact number should be determined from industry segmentation, based on the overall industrial category (phosphorus production, etc.), geographical location (annual rainfall), and product mix (particularly few-product versus many-product plants). For each sub-category, BPT is double liming plus vacuum filtration.

The guidelines for PCl_3 and $POCl_3$ appear to be correct, as do the Level II and III guidelines. BPT for T.D.S. (total dissolved solids) is not at all clearly established in the memorandum.

The basis for the cost estimates presented in the "Proposed Effluent Limitations ..." Action Memorandum is Supplement A to the Draft Report prepared by General Technologies Corporation, summarized in Tables 17 and 18 of the Development Document dated August 23, 1973. Supplement A consists of one table for each segment of the industry; blanks are filled in on each table - for example, for the "Manufacture of Phosphorus" segment of the industry a single number of $500,000 is written for piping, pumping, and controls equipment for 100% recycle of process wastewater to the head end of the plant - with no further breakdown, justification, or defense. On the basis of the cost

information presented, it is impossible to judge the merit of that figure, or of any other figures presented in Supplement A. All cost data in Table V of the Action Memorandum are derived from the non-substantiated figures in Supplement A.

Phosphates

STATE OF FLORIDA
DEPARTMENT OF POLLUTION CONTROL
2562 EXECUTIVE CENTER CIRCLE, EAST
MONTGOMERY BUILDING, TALLAHASSEE, FLORIDA 32301

July 31, 1973

PETER P. BALJET
EXECUTIVE DIRECTOR

DAVID H. LEVIN
CHAIRMAN

Mr. Allen Cywin, Director
Effluent Guidelines Division
United States Environmental Protection Agency
Washington, D.C. 20460

Dear Mr. Cywin:

This will acknowledge receipt of the draft industrial effluent guidelines for a number of industries. Of those received, the following have not been commented upon because they are not present in Florida, or because our experience with them has been very limited:

a. Leather tanning and finishing.

b. Grain mills.

c. Soap and detergent manufacturing.

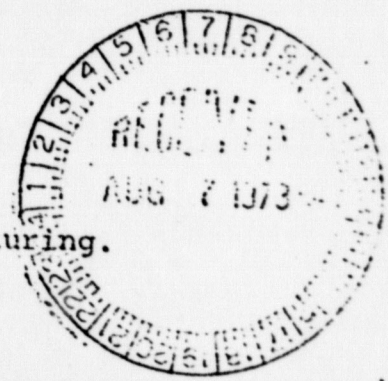
d. Non-ferrous metals (aluminum) manufacturing.

e. Ferroalloy manufacturing.

f. Flat glass manufacturing.

g. Asbestos manufacturing.

h. Inorganic chemicals, alkali and chlorine industries.



The quality of the reports varied considerably with the consultant. Most provided a reasonable collection of information on the state-of-the-art in controlling the subject effluent load. Comments on the reports reviewed by the Department staff follow:

It is recommended that the reports present the data in English terms, such as pounds of BOD_5, with the accompaning metric term. Further, the standards should be in units per unit of product, such as lbs.BOD_5/ 1,000 lbs live weight.

That is, the effluent guidelines in some instances and those in the "Interim Guidelines for NPDES" are not consistent with respect to the discharge basis. For example, one set of guidelines uses pounds of pollutants per gallon of waste, while the other uses pounds of

W. R. MIDDLEMAS
BOARD MEMBER
GEORGE RUPPEL
BOARD MEMBER
JAMES F. REDFORD, JR.
BOARD MEMBER
W. D. FREDERICK, JR.
BOARD MEMBER

2. Fertilizer and Phosphate Manufacturing

The recommended guidelines are acceptable to the State of Florida. The State objectives are to obtain lower levels than those recommended. A level of 1.0 mg/l of ortho phosphate was recommended to the industry, but is yet unachieved. However, it is believed possible to have self-contained systems and several processors have achieved this most of the time.

As to the floride level, the State standard is 10 mg/l after reasonable mixing. Thus, an effluent level of 15 mg/l would appear to be reasonable.

Nitrogen levels expressed for level I as "N" not $NH_3(NH_3)_2NO_3$ or urea are acceptable.

The effluent standards now applicable to municipal wastes discharging to certain waters of the State require Advanced Waste Treatment with effluent levels of 3 mg/l total nigrogen as N and 1 mg/l phosphorous as P. These have not been considered for application to industrial sources, but lower limits than those in the report would probably be required.

One would expect the proposed Level III Guidelines for the nitrogen fertilizer industry to be more restrictive than for Level II (Page II-3, II-4).

3. Non-Fertilizer Phosphorous Chemicals Industry

The recommendations appear satisfactory and there is nothing in the State's experience to suggest other standards.

4. Meat Packing Industry

This report could benefit through careful editing to reduce duplication of material. Recommendations for 1977 (Level I) appear reasonable. The recommendations for 1983 appear to be achievable, but it is believed that the costs to accomplish this will be several magnitudes greater.

It is suggested that consideration be given to positive pressure chlorination of the effluent with at least 30 minutes retention and a chlorine residual of 0.5 mg/l. Further, limits should be considered for the chemical ions (such as chlorides) resulting from the use of preservatives.

ILLINOIS ENVIRONMENTAL PROTECTION AGENCY

2200 Churchill Road
62706

Springfield, Illinois
Phone: (312) 793-5632

Martin

August 1, 1973

Federal Draft Effluent Guidelines - Non-Fertilizer Phosphorus Chemicals Industry

RECEIVED
AUG 6 1973

U. S. Environmental Protection Agency
Regional Administrator
Region V
1 North Wacker Drive
Chicago, Illinois 60606

Attn.: James McDermott

Gentlemen:

Following are comments relative to the above guidelines draft which should be considered prior to adoption. These are being brought to your attention pursuant to the June 29, 1973 letter, from Mr. Allen Cywin, Addressed to Director Marco:

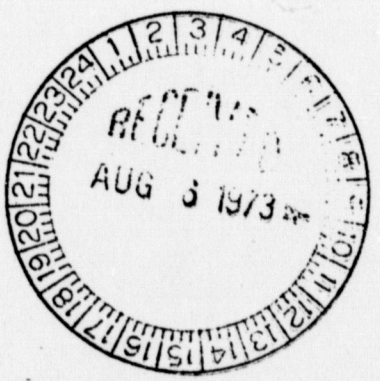
1. The recommended Level I guideline of zero discharge for process waters from the entire industry (except for PCl_3 and $POCl_3$) is acceptable.

2. The Level I guidelines for PCl_3 and $POCl_3$ process waters are listed in pounds of parameter (total suspended solids, and total dissolved solids), per ton and kilograms of parameter per metric ton of product produced. This does not reflect an effluent concentration. Limiting values for the effluent concentrations of the above listed parameters must be established.

3. The Level I guideline for the pH in the process waters from the manufacture of PCl_3 and $POCl_3$ appears to be slightly high. A more appropriate value would be a pH value of 9 or 10. Also, the pH limitation should not be subject to averaging and must be met at all times.

4. No water quality consideration has been given with respect to any of the above listed parameters nor phosphorus or chlorides.

The following critique represents the views of the Izaak Walton League of America regarding proposed recommendations for effluent guidelines and standards of performance for the non-fertilizer phosphorus chemicals industry. Because of time limitations given for submission of comments, we were unable to receive more than superficial comments on this report. Those individuals, invited by the League to comment on the engineering aspects of this industry were particularly pressed by unanticipated work loads at their regular jobs. As a result, this summary does not meet our normal standards and should not be considered as conclusive. If our organization receives additional reviews in the next few days, we will be happy to send these along with our comments.



(d) cluding methods of reporting and monitoring for:

(1) process upsets caused by accidents or weekend and/or holiday shutdowns or start ups
(2) production rate changes
(3) changes in product mix
(4) seasonal variations in waste concentrations and flow volume

Appendix B Suggested Standards of Performance for New Sources

B. Standard of performance required for each such category

3. The factors which should be taken into account in determining level II control and treatment technology for particular plants and consequently in determining permissable effluent levels for such plants.

C. Sampling, analytical techniques and monitoring requirements

1. Sampling required to be conducted on discharges by sample type, frequency, and location points including:

(a) critical waste parameters
(b) secondary waste parameters
(c) sampling point
(d) reporting and monitoring requirements including reporting and monitoring requirements with allowances for:

(1) process upsets caused by accidents or weekends and/or holiday shutdowns and start ups
(2) production and rate changes
(3) changes in product mix
(4) seasonal variations in waste concentrations in flow volume

2. Techniques for analyzing samples taken, including bioassays, where applicable

II.

Both those consultants with an academic knowledge of this industry and those consultants in administrative positions in pollution control agencies agreed that recommended level I guidelines for manufacturing plants of phosphoric acid, sodium tripolyphosphate, animal feed grade calcium phosphate and those in the phosphorus production segment were both reasonable and

Monsanto

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

July 18, 1973

Dr. Robert G. Shaver
President
General Technologies Corporation
6621 Electronic Drive
Springfield, Virginia 22151

Dear Bob:

You will, in the next few days, be receiving Monsanto's formal comments on the non-fertilizer phosphorus chemicals effluent guidelines study over the signature of our Mr. C. P. Cunningham, Vice President and Managing Director of the Industrial Chemicals Company. For obvious reasons we did not go into page by page detail in these comments. For what they're worth, therefore, these comments are itemized below.

Section I, Page 2, Paragraph 2 states that the phosphates segment is characterized by acids and finely divided solids. Recommend adding dissolved solids.

It is stated that several plants (STP and calcium phosphates) have already achieved zero discharge by in-process controls and end of process treatment. Based on our telephone conversation last week, I understood that your zero discharge recommendations in this category were based on our Trenton, Michigan lime precipitation technology. This process is not zero discharge. The resulting solution of sodium hydroxide and excess lime in the form of dissolved solids is unsuitable for recycle back into our multi-product and food-grade plant. We question, therefore, whether zero discharge is, in fact, demonstrated in all these processes.

Section II, Page 3 - Pretreatment standards called for zero dissolved solids for those products with a zero discharge limitation. This would effectively prohibit continued participation in public treatment which is contrary to the intent of the FWPCA Amendments of 1972.

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The 250 ppm maximum total suspended solids limitation again would prohibit removal of these solids by public treatment works on a surcharge basis. We see no justification for this recommendation.

The 30 ppm total phosphate limit on an across-the-board basis is likewise unnecessary. Such limits should depend on whether any eutrophication potential exists in the particular watershed and whether the municipal system is practicing phosphorus removal.

Section III, Page 6 - Tennessee washer tailings practiced suggests a number more like 9,000 kilograms of tails/kkg of phosphorus.

Section IV, Page 1 - Again, sodium and calcium phosphates are characterized by dissolved solids as well as "finely divided solids."

Section IV, Page 3 - We are of the opinion that electrostatic precipitation of kiln off-gas dust is the exception, rather than the rule. Most use mechanical collectors, wet scrubbers, or a combination of the two.

Section IV, Page 5. The current loading for a furnace electrode in the 5 to 6 ft. diameter range would be considerably in excess of 50,000 amps.

We are unaware of any use for water to cool electrode joints. The electrode holder mechanisms are generally water-cooled, however.

We are of the opinion that neither of the two rotating crucible furnaces in existence (Monsanto's Soda Springs, Idaho and TVA's Muscle Shoals, Alabama) are utilizing this feature.

The comment regarding vanadium content of ferro-phosphorus is probably applicable only to western ores.

Section IV, Page 6. The comment that no water is involved in ferro-phosphorus "subsequent product preparation" should be modified to recognize the possible use in wet-type dust collectors or water separation equipment. We do not currently utilize either, but have used both.

The statement regarding a high velocity water stream for producing granulated slag is correct; however, expanded slag is produced by introducing the molten slag into a standing excess quantity of water.

Section IV, Page 7, Paragraph 2 - Natural gas should be added to the means of heating electrostatic precipitator jackets.

Section IV, Page 9 - Fiber-type mist eliminators should be added to electrostatic precipitators as a means of collecting phosphoric acid mist. The fiber-type units are probably the most common approach at this point in time.

Section V, Page 33. We were surprised to see that you concluded from our Soda Springs non-contact cooling water data that pH "can be controlled more closely than other parameters" since there is no pH control exerted on this stream. We suggest that analysis of a waste stream, where some neutralization is required, would be more meaningful.

Section VI - 3. We are of the opinion that fluorides are present in natural waters in concentrations as high as 8 ppm.

Section VII, Page 1. We're not entirely sure what is meant by "in excess of natural proportion in phosphorus compounds" relative to arsenic.

Section VII, Page 2 - 2.1. Incoming pure water?

Section VII, Page 8. In cases where large surface area quiescent settling is necessary to control very fine suspended solids (i.e. turbidity), your statement that allowing overflow in times of heavy rainfall "represents poor effluent control" is questionable. Proper design of the pond, particularly relative to the depth of clear water maintained on top of the settling zone, can virtually eliminate any loss of pollutants during times of necessary overflow.

Section VII, Page 13. This treatment of phossy water processing by liming and subsequent settling/evaporation overlooks an inherent problem of P_2O_5 and phosphine fuming.

Section IX, Page 5 states that the exemplary phosphorus plants "treatment system" overflows in times of high rainfall. Combining this statement with the one previously referred to in Sec. VII, Page 8, indicates that the exemplary plant "represents poor effluent control."

Section IX, Page 5 - it is our understanding that the granulated slag produced by TVA has a very limited market as opposed to the hard aggregate produced by other phosphorus manufacturers. This by-product credit consideration is no problem to TVA who has very little cost reduction motivation.

The statement that "there is no requirement to bleed off water for the control of dissolved solids" implies that residual dissolved solids presents no problem after lime treatment. It should be emphasized in this context as well as relative to the lime phosphate removal process that you are simply substituting one dissolved solid for another, and not "controlling dissolved solids."

The last paragraph states that "Tables 11 and 12 lists the effluent concentrations and quantities discharged from these plants (Columbia and Soda Springs), neither of which recycle treated waste water. This is a totally

incorrect statement. Both of these plants extensively recycle all phossy water and all kiln scrubber water. In fact, the only process streams not recycled are the raw material dust collector effluent and slag quenching water at Plant 028 only.

Section IX, Page 8 states that Soda Springs "intakes ground water and discharges in the surface water so that its responsibility is to gross amount of constituent quantities." We see no justification for this definition in the report.

We do not understand the paragraph that begins "the above three differences are interrelated and affect the quantities..."

Freezing problems of cooling towers was not included in your discussion of cold weather total recycle problems.

Section IX, Page 10 states "...in view of the existence of two plants (TVA and 181) which have already achieved zero discharge of other process waters..." Discussions with TVA this week suggest that this is an incorrect statement. I have attached a block diagram of TVA's aqueous wastes which indicate that their phossy water system, precipitator dust system, and fluorine liquor system are all tied together and discharged through settling ponds to the Tennessee River. We are amazed that such a conclusion would be included in the report without verification. TVA was unaware of any inquiry on this subject.

Section IX, Page 13 states that "exemplary plant 042 has no process wastes." The discussion does not state, however, whether this is a solution feed or slurry feed process. The former, in our estimation, can readily achieve zero process discharge, whereas the latter cannot.

Section IX, Pages 14 - 16 deals with food-grade calcium phosphates. This discussion transfers phosphate removal technology from our Michigan sodium phosphate plant to our St. Louis calcium phosphates plant. We have no experience with lime precipitation on calcium phosphate wastes. In any case, the statement on Page 16 that this process is capable of removing phosphates to a level of 0.5 ppm came from early prototype published data. We made a specific point to emphasize to your investigator that subsequent experience found that treatment to such a level required extensive quiescent settling beyond the real estate available. Accordingly, we converted to vacuum filtration which, although achieving 95% removal, involves effluents in the 50-150 ppm range. The reference to use of polymeric flocculents in municipal waste water treatment appears inappropriate in this discussion.

The conclusion that "the treated waste water from the manufacture of food-grade calcium phosphates then is certainly pure enough to be re-used as input process water" is unjustified. We feel that substantial additional filtration, ion exchange, purification, and possibly sterilization would be necessary. Further, the statement that "once the commitment to a total recycle is made, the lime treatment step may be by-passed" is unsubstantiated and in fact, unbelievable.

Here are several late comments inserted out of page order.

Section III - 6. Paragraph 2 states that much of the furnace phos acid is directly marketed. We believe that this amounts to less than 10%.

Paragraph 5 refers to "wooled phosphate rods." Should this have read "washed phosphate ore"?

Section IX, Page 11-3 2.4. The exemplary P_2S_5 operation did not concern itself with dust collection from P_2S_5 milling and packaging operations. It superficially treated the casting of blocks or cones of P_2S_5 under an inert atmosphere but did not make ultimate disposal of the P_2S_5 picked up by the inert gas. As an alternate approach, the recommendation is to use dilute lime as a scrubbing media, followed by settling of particles and precipitates of calcium salts. The clear water would be circulated back to the system.

In our opinion the primary recommendations for eliminating effluent from P_2S_5 operations are based on an underestimation of the problem. For milled product, a major product form, returnable containers must be thoroughly cleaned. Liners or disposable containers make a serious disposal problem. Dust and fume collection from various operations must be handled effectively to control H_2S generation. Dry dust collection systems are, in our experience, unsafe for P_2S_5.

The alternate approach is generally acceptable but some purge from the system would be expected. Accordingly we do not feel the proposed technology warrants a zero discharge recommendation.

In the light of the above comments, combined with those in our more formal statement to EPA and the Effluent Guidelines Advisory Committee, it would appear that our decision to cooperate in this study was ill-advised. The information which supported the apparently preconceived conclusion of zero discharge was used and re-used. Information which contradicted zero discharge philosophy was ignored. Accordingly, I

have recommended to my management that we not participate in future effluent studies conducted by General Technologies.

Very truly yours,

M. L. Mullins
Manager
Environmental Protection

MLM:ms

Enc.

cc: Mr. D. B. Hosmer
Monsanto - St. Louis, Mo.

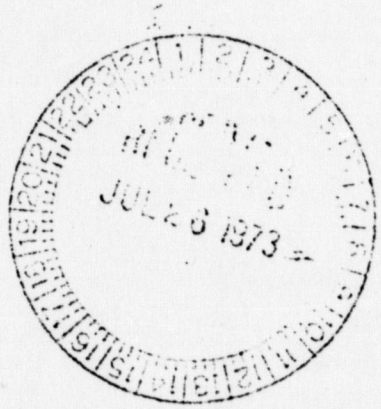
Mr. Elwood E. Martin
Project Officer
EPA Effluent Guidelines Div.
Washington, D. C. 20460

From Estes 9/4/73

Monsanto

Monsanto Industrial Chemicals Co.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone (314) 694-1000

July 20, 1973



Dr. Martha Sager
Chairman, Effluent Standards
& Water Quality
Information Advisory Committee
Environmental Protection Agency
Room 821, Crystal Mall-Bldg. #2
Washington, D. C. 60460

Dear Dr. Sager:

Monsanto Company appreciates the opportunity to comment on the General Technologies Corporation draft contractors' report ("Development Document for Effluent Guidelines and Standards of Performance for the [redacted] Fertilizer Phosphorus Chemicals Industry", dated June, 1973).

In this discussion, I would first like to have you consider with me some very serious questions I have about the intent and methodology described in the Development Document. Then, I would like to present several preliminary recommendations of my own.

Question: Are the zero-discharge limitations premature? Are they fair? Are they based on fact?

The report recommends zero discharge of process water for six of eight products in the study.

Is this premature? It certainly is, if you assume (as we do) that zero discharge represents "best available technology". "Best available" is sought by 1983, according to Public Law 92-500. No mention of total elimination or zero discharge is made about 1977 performance. The same Act, in Section 301b (1) and (2), states that total elimination of pollutants in a discharge may be required by 1983, if the technology is available. The Development Document's blanket requirement for zero discharge, to be achieved by 1977, must be considered as premature.

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Is this fair? It certainly is not, if you recognize the elaborate end-point treatment facilities installed at numerous plants. The report itself notes several such examples of high removal efficiencies:

"Plants 028 and 159 achieve very high (97-99%+) control and treatment efficiencies and correspondingly low quantities (although not absolutely zero) of discharged constituents." It also points (in Section IX, Pages 15 and 16) to an elaborate phosphate removal process involving lime treatment, clara-flocculation and direct vacuum filtration as "achieving extremely low levels of total suspended and dissolved solids".

Requiring these kinds of operations to achieve zero discharge will mean abandonment or costly modification of very efficient end-point treatment. It will also mean a significant new capital investment for a very insignificant improvement.

We would assume the companion economic impact study (now being undertaken by Arthur D. Little & Co.) would reflect this. It is our understanding, however, that compliance costs have been prescribed in Supplement "A" of the total report (not released for comment), and is not to be further investigated. We also understand that the cost estimates per plant are in the 0-$500M range. Compared to our preliminary estimates, this is an order of magnitude low.

Are the zero-discharge limitations technically realistic? We have enough concern to at least pose the question.

For example:

In justifying zero process discharge for phosphorus manufacture, the report states that the Tennessee Valley Authority has achieved total recycle of process streams other than phossy water. We have talked to TVA, and they tell us that their three process water streams (phossy water, precipitator dust slurry, and kiln scrubber systems) jointly discharge to the Tennessee River.

The justification for zero discharge for food-grade calcium phosphates is based on Monsanto's St. Louis operation. The report uses our raw-waste-load data, and then cuts the data in half (based on our plans to convert from wet scrubbers to bag collectors). On top of that, however, is applied sodium phosphate removal technology from our Trenton, Michigan plant. From that, a 0.5 ppm effluent (rather than the 50-100 ppm actual performance) is established. Finally, the report introduces further

undemonstrated technology by supposing that polymeric flocculation data from EPA's municipal phosphorus removal test could also be applied to this stream. The resulting hypothetical stream would be good enough to recycle back into the food-grade process, the Document concluded.

Speaking from a very extensive manufacturing background, we at Monsanto know that lime precipitation of calcium phosphates is highly questionable. We know the resulting chemistry would create insurmountable quality problems. And we know that the cost of additional filtration, demineralizing, and sterilization necessary to re-use the water would be enough to economically drown the operation.

Other questions about the feasibility of zero discharge by 1977 arise in connection with the unique problems of multi-product plants, food-grade operations, product mix restraints, and process variations such as solution feed vs. slurry feed. Imagine the technical nightmare of trying to recycle the right material to the right process when the same plant produces several different products simultaneously, and at different times, and uses a multitude of raw materials showing up in the effluent stream. These considerations were not reflected in the report.

Finally, no consideration was given to resultant air-quality or solid-waste problems. These include P_2O_5 and phosphine fumes from lime treatment and oxidation of phossy water, and disposal of high-moisture content sludge resulting from phosphate removal.

So to answer my own questions, I think the zero-process discharge recommendations are premature, unfair to "good-faith" manufacturers, and at least in some instances, not technically realistic. They also do not consider the differences among plant operations. They go far beyond the intent of Congress.

Question: Are the proposed pretreatment requirements realistic, or desirable in all cases?

The report recommends pretreatment standards which include total dissolved-solids limitations "the same as the applicable levels I, II, or III Effluent Limitation Guidelines". In most cases, this would be zero!

By thus requiring total recycle, this provision would eliminate any industrial participation in Public Treatment Systems!

The proposed standards allow maximum total suspended solids of 250 ppm and maximum concentrations of total phosphates (as PO_4) of 30 ppm. On a surcharge basis, several Monsanto locations now pay municipal treatment systems to remove our suspended solids. This is obviously more economical to us. But it also means lower costs to municipal-system customers, where these systems can attain economies of scale.

The 250 ppm limit also appears to contradict previous EPA guidelines. The EPA has repeatedly stated there will be no Federal pretreatment requirements for "compatible pollutants," such as suspended solids. The proposed limits on total phosphates also appear to be contradictory to the report's own requirement of zero total dissolved solids, and to EPA's stance that phosphate and its role as a nutrient should be considered a local problem, where across-the-board limits are unwise and unnecessary.

Question: What is a violation of a zero limitation?

Frankly, I can't answer this question, based on the report. There is no recognition of the variability of incoming water or of the limits of prescribed analytical techniques.

Question: Is there to be no allowable discharge of well water?

Apparently not, in most cases. On Page IX-8, it states that "Plant 159 intakes ground water and discharges into surface water so that its responsibility is the gross amount of constituent quantities". This could mean that for a plant with a zero-process-discharge guideline, there is to be no discharge of any well water into a surface stream. This requirement is not justified in the report, and is not consistent with IX-2-2.0, which allows discharge of non-contact cooling water.

In addition, such a requirement would actually cause deterioration in surface water quality (in Plant 159 and other cases where well quality is superior to surface water). In cold-climate areas, it would cause severe operating problems. And it would deprive downstream users of accustomed and valuable water use rights.

We therefore recommend, and have recommended many times before, that the discharge of well water be considered on a case-by-case basis, and that any requirement recognize the relative quality of the well water and the surface stream involved.

RECOMMENDATIONS:

I would like to present some preliminary recommendations here:

- That 1977 effluent limits be established for elemental phosphorus plants which allow continued use of existing effective, elaborate, and expensive water quality programs short of zero discharge. Limits of 1 lb/ton T.S.S.; 10 lbs/ton T.D.S.; 0.4 lbs/ton fluoride; 0.35 lbs/ton total phosphate and zero elemental phosphorus are suggested.

- That food-grade and multi-product phosphate salts plants be excluded from the proposed guidelines pending further study.

- That pretreatment guidelines address only incompatible pollutants.

- That discharge of well water be governed on a net effluent quantity basis unless local water quality requirements require more restrictive limitations.

IN CONCLUSION:

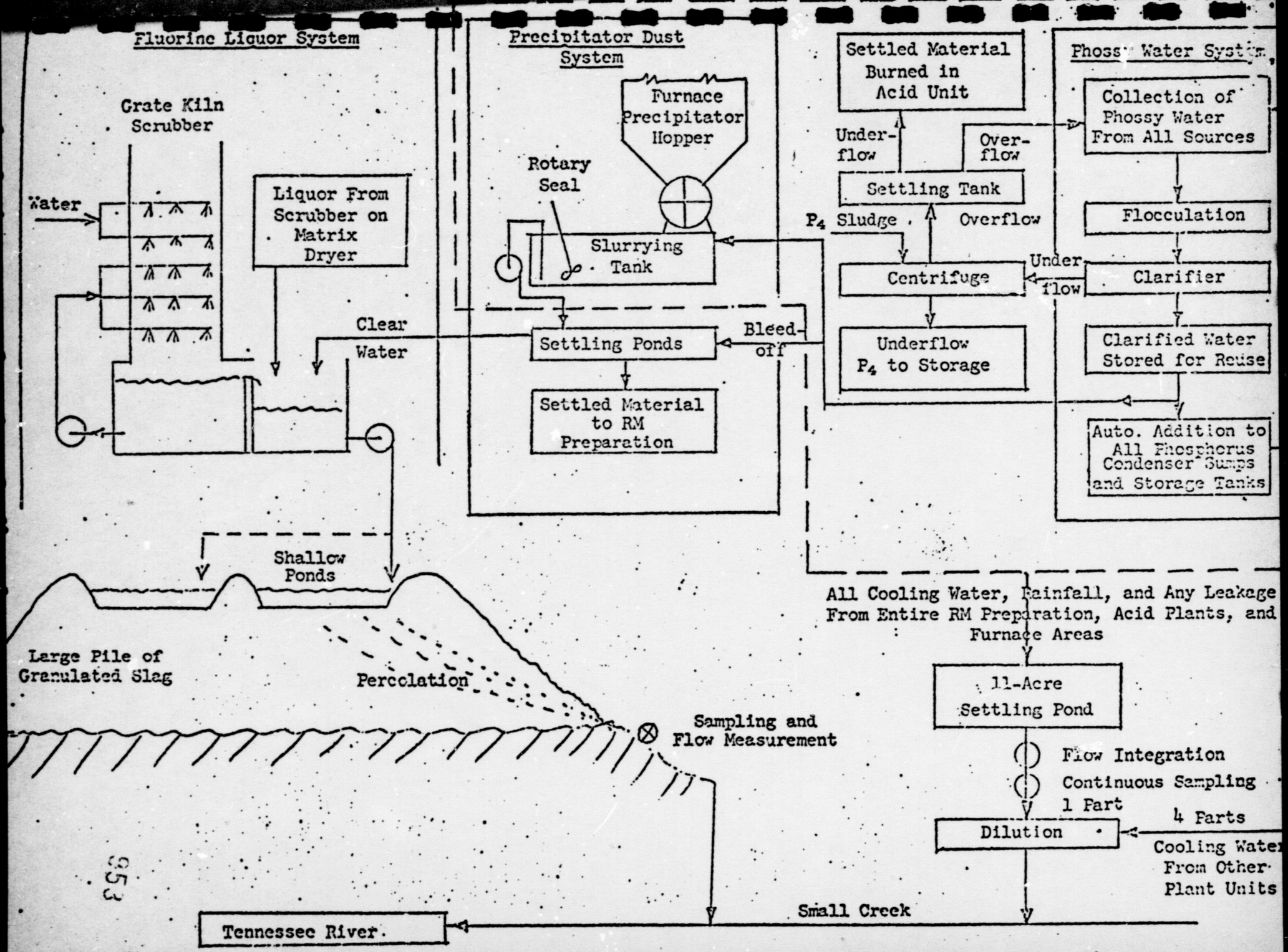
Monsanto has continually demonstrated its "good faith" in helping improve its water effluents. Realistic standards will pose no undue economic or technical obstacles to us. They will also prompt "laggers" to action. Unrealistic standards - as we feel the report presents - will produce innumerable delays as they are debated, argued, discussed, thereby deferred. This benefits no one.

We strongly urge reconsideration of the points discussed above. We stand ready to work with EPA, the Advisory Committee, and/or EPA's contractors to this end. More detailed page-by-page comments have been prepared and will be transmitted separately to EPA by August 1.

Again, we appreciate the opportunity to participate in this rule-making process.

M. L. Mullins
Manager
Environmental Protection

MLM:ms



CONTROL OF AQUEOUS WASTES IN TVA PHOSPHORUS PLANT

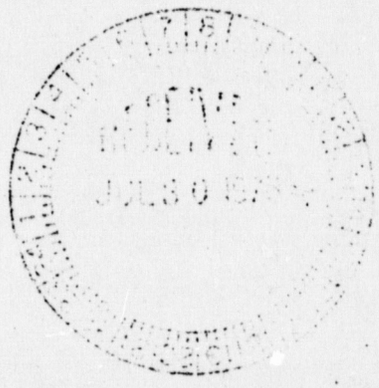
Martin

Monsanto

C. P. CUNNINGHAM
Vice President
A Monsanto Company

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-2000

July 20, 1973



Mr. Allen Cywin
Director, Effluent Guidelines Division
Environmental Protection Agency
Waterside Mall
Washington, D. C. 20460

Dear Mr. Cywin:

Attached for your information is a copy of a statement for submission by Monsanto to the Effluents Standards & Water Quality Information Advisory Committee on July 24. These remarks reflect Monsanto's position relative to the draft report on Effluent Guidelines for the New Fertilizer Phosphorus Chemicals Industry.

Your earnest consideration of these comments prior to publishing proposed effluent standards is requested.

Please let us know if we can be of assistance.

Very truly yours,

C. P. Cunningham
Managing Director,
Vice President

Enc.

cc: Mr. William Driver, President
Manufacturing Chemists Association
1825 Connecticut Ave., N.W.
Washington, D. C. 20009

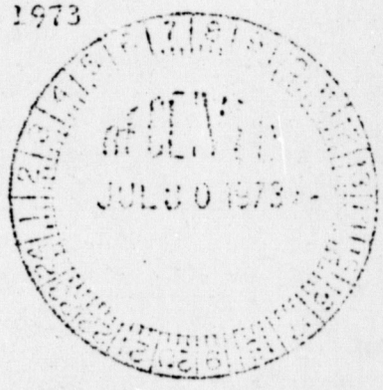
Dr. Robert Shaver, President
Arapol Technologies Corporation

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Monsanto

MONSANTO INDUSTRIAL CHEMICALS CO.
800 N. Lindbergh Boulevard
St. Louis, Missouri 63166
Phone: (314) 694-1000

July 20, 1973



Dr. Martha Sager
Chairman, Effluent Standards
& Water Quality
Information Advisory Committee
Environmental Protection Agency
Room 821, Crystal Mall-Bldg. #2
Washington, D. C. 60460

Dear Dr. Sager:

Monsanto Company appreciates the opportunity to comment on the General Technologies Corporation draft contractors' report ("Development Document for Effluent Guidelines and Standards of Performance for the Non-Fertilizer Phosphorus Chemicals Industry", dated June, 1973).

In this discussion, I would first like to have you consider with me some very serious questions I have about the intent and methodology described in the Development Document. Then, I would like to present several preliminary recommendations of my own.

Question: Are the zero-discharge limitations premature? Are they fair? Are they based on fact?

The report recommends zero discharge of process water for six of eight products in the study.

Is this premature? It certainly is, if you assume (as we do) that zero discharge represents "best available technology". "Best available" is sought by 1983, according to Public Law 92-500. No mention of total elimination or zero discharge is made about 1977 performance. The same Act, in Section 301b (1) and (2), states that total elimination of pollutants to a discharge may be required by 1983, if the technology is available. The Development Document's blanket requirement for zero discharge, to be achieved by 1977, must be considered as premature.

Is this fair? It certainly is not, if you recognize the elaborate end-point treatment facilities installed at numerous plants. The report itself notes several such examples of high removal efficiencies:

"Plants 028 and 159 achieve very high (97-99%+) control and treatment efficiencies and correspondingly low quantities (although not absolutely zero) of discharged constituents." It also points (in Section IX, Pages 15 and 16) to an elaborate phosphate removal process involving lime treatment, clarafloccultation and direct vacuum filtration as "achieving extremely low levels of total suspended and dissolved solids".

Requiring these kinds of operations to achieve zero discharge will mean abandonment or costly modification of very efficient end-point treatment. It will also mean a significant new capital investment for a very insignificant improvement.

We would assume the companion economic impact study (now being undertaken by Arthur D. Little & Co.) would reflect this. It is our understanding, however, that compliance costs have been prescribed in Supplement "A" of the total report (not released for comment), and is not to be further investigated. We also understand that the cost estimates per plant are in the 0-$500M range. Compared to our preliminary estimates, this is an order of magnitude low.

Are the zero-discharge limitations technically realistic? We have enough concern to at least pose the question.

For example:

In justifying zero process discharge for phosphorus manufacture, the report states that the Tennessee Valley Authority has achieved total recycle of process streams other than phossy water. We have talked to TVA, and they tell us that their three process water streams (phossy water, precipitator dust slurry, and kiln scrubber systems) jointly discharge to the Tennessee River.

The justification for zero discharge for food-grade calcium phosphates is based on Monsanto's St. Louis operation. The report uses old raw waste-load data, and then cuts the data in half (based on our plans to convert from wet scrubbers to bag collectors). On top of that, it is applied sodium phosphate removal technology from our Trenton, Michigan plant. From that, a 0.5 ppm effluent (vs. less than the 50-100 ppm actual performance) is established. Finally, the report introduces further

undemonstrated technology by supposing that polymeric flocculation data from EPA's municipal phosphorus removal test could also be applied to this stream. The resulting hypothetical stream would be good enough to recycle back into the food-grade process, the Document concluded.

Speaking from a very extensive manufacturing background, we at Monsanto know that lime precipitation of calcium phosphates is highly questionable. We know the resulting chemistry would create insurmountable quality problems. And we know that the cost of additional filtration, demineralizing, and sterilization necessary to re-use the water would be enough to economically drown the operation.

Other questions about the feasibility of zero discharge by 1977 arise in connection with the unique problems of multi-product plants, food-grade operations, product mix restraints, and process variations such as solution feed vs. slurry feed. Imagine the technical nightmare of trying to recycle the right material to the right process when the same plant produces several different products simultaneously, and at different times, and uses a multitude of raw materials showing up in the effluent stream. These considerations were not reflected in the report.

Finally, no consideration was given to resultant air-quality or solid-waste problems. These include P_2O_5 and phosphine fumes from lime treatment and oxidation of phossy water, and disposal of high-moisture content sludge resulting from phosphate removal.

So to answer my own questions, I think the zero-process discharge recommendations are premature, unfair to "good-faith" manufacturers, and at least in some instances, not technically realistic. They also do not consider the differences among plant operations. They go far beyond the intent of Congress.

Question: Are the proposed pretreatment requirements realistic, or desirable in all cases?

The report recommends pretreatment standards which include total dissolved solids [illegible] "the same as the applicable levels I, II, or III effluent Limitation Guidelines". In most cases, this would be

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By this requiring joint projects, this would [illegible] eliminate any [illegible] provided [illegible] Public Treatment Systems.

The proposed standards allow maximum total suspended solids of 250 ppm and maximum concentrations of total phosphates (as PO_4) of 30 ppm. On a surcharge basis, several Monsanto locations now pay municipal treatment systems to remove our suspended solids. This is obviously more economical to us. But it also means lower costs to municipal-system customers, where these systems can attain economies of scale.

The 250 ppm limit also appears to contradict previous EPA guidelines. The EPA has repeatedly stated there will be no Federal pretreatment requirements for "compatible pollutants," such as suspended solids. The proposed limits on total phosphates also appear to be contradictory to the report's own requirement of zero total dissolved solids, and to EPA's stance that phosphate and its role as a nutrient should be considered a local problem, where across-the-board limits are unwise and unnecessary.

Question: What is a violation of a zero limitation?

Frankly, I can't answer this question, based on the report. There is no recognition of the variability of incoming water or of the limits of prescribed analytical techniques.

Question: Is there to be no allowable discharge of well water?

Apparently not, in most cases. On Page IX-8, it states that "Plant 159 intakes ground water and discharges into surface water so that its responsibility is the gross amount of constituent quantities". This could mean that for a plant with a zero-process-discharge guideline, there is to be no discharge of any well water into a surface stream. This requirement is not justified in the report, and is not consistent with IX-2-2. 0, which allows discharge of non-contact cooling water.

In addition, such a requirement would actually cause deterioration in surface water quality (in Plant 159 and other cases where well quality is superior to surface water). In cold-climate areas, it would cause severe operating problems. And it would deprive downstream users of accustomed and valuable water use rights.

We therefore recommend, and have recommended many times before, that the discharge of well water be considered on a case-by-case basis, and that any requirement recognize the relative quality of the well water and the surface stream involved.

RECOMMENDATIONS:

I would like to present some preliminary recommendations here:

- That 1977 effluent limits be established for elemental phosphorus plants which allow continued use of existing effective, elaborate, and expensive water quality programs short of zero discharge. Limits of 1 lb/ton T.S.S.; 10 lbs/ton T.D.S.; 0.4 lbs/ton fluoride; 0.35 lbs/ton total phosphate and zero elemental phosphorus are suggested.

- That food-grade and multi-product phosphate salts plants be excluded from the proposed guidelines pending further study.

- That pretreatment guidelines address only incompatible pollutants.

- That discharge of well water be governed on a net effluent quantity basis unless local water quality requirements require more restrictive limitations.

IN CONCLUSION:

Monsanto has continually demonstrated its "good faith" in helping improve its water effluents. Realistic standards will pose no undue economic or technical obstacles to us. They will also prompt "laggers" to action. Unrealistic standards - as we feel the report presents - will produce innumerable delays as they are debated, argued, discussed, thereby deferred. This benefits no one.

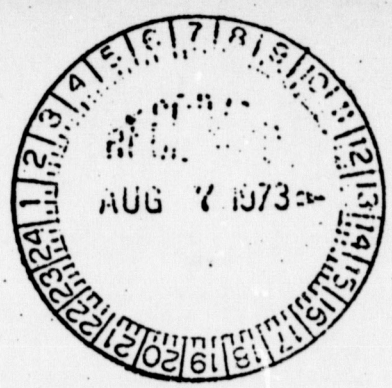
We strongly urge reconsideration of the points discussed above. We stand ready to work with EPA, the Advisory Committee, and/or EPA's contractors to this end. More detailed page-by-page comments have been prepared and will be transmitted separately to EPA by August 1.

Again, we appreciate the opportunity to participate in this rule-making process.

959

M. L. [illegible]
Manager
Environmental Protection

ML:[illegible]



Martin
Ea.

OFFICE OF WATER AND AIR RESOURCES

July 23, 1973

Regional Administrator
Region IV
United States Environmental
Protection Agency
1421 Peachtree Street, NE.
Atlanta, Georgia 30309

SUBJECT: Draft Report
Effluent Limitations
Guidelines, Non-Fertilizer
Phosphorus Industry

Dear Sir:

The Draft Report for Effluent Limitations Guidelines for the non-fertilizer phosphorus industry prepared by General Technologies Corporation has been reviewed by members of the staff of this Office.

This report proposes that Best Practible Control Technology Currently Available would result in zero discharge of process waters from all manufacturing operations except the production of phosphorus trichloride and phosphorus oxychloride, and the discharge of cooling water under controlled and specified conditions. Discharges from the production of phosphorus trichloride and phosphorus oxychloride would be allowed to contain specified amounts of suspended and dissolved solids. The specified amounts of suspended and dissolved solids appears to be reasonable and acceptable. However, the specified allowable pH (6.0 - 10.5) is not acceptable and should be changed to 6.0 - 9.0.

Best Available Technology Economically Attainable will result in zero discharge of process waters but will allow discharge of cooling water under specified conditions, which are acceptable. However, the provision of monitoring for process leaks and provision of emergency holding facilities for contaminated cooling water should be required as Level I (Best Practible Control Technology Currently Available) instead of Level II (Best Available Technology Economically Attainable) control.

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We appreciate the opportunity of reviewing these reports. Please do not hesitate to call on us if we can be of further service.

Sincerely,

E. C. Hubbard
Assistant Director

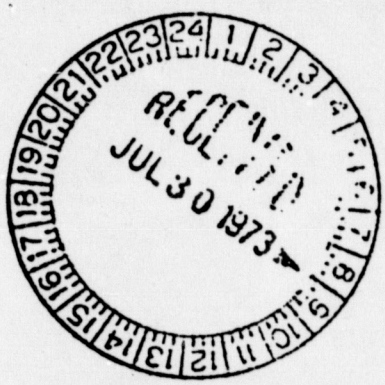
ACT/fhe

cc: Mr. Allen Cywin
Mr. L. P. Benton, Jr.
Eastern Regional Office

DEPARTMENT OF ENVIRONMENTAL PROTECTION
AUGUSTA, MAINE 04330

July 24, 1973

'AN R. ADAMS, JR.
COMMISSIONER



Mr. John A. McGlennon
Regional Administrator
Region I
Environmental Protection Agency
J.F.K. Federal Building
Boston, Mass 02203

SUBJECT: Effluent Guidelines

Dear Mr. McGlennon:

Due to ever increasing material from EPA for review and the very short time allotted for this review together with our usual workload a thorough evaluation of the material has not been possible. In general we agree with the author's findings but reserve the right to implement and enforce State of Maine laws and State, local, and departmental regulations and policies where applicable.

Received June 27. Date for Comment, July 25, 1973

Timber Products Industry: No comment
Organic Chemicals Industry: No comment
Plastics and Synthetics Industry: No comment
Cement Mfg. Industry: No comment

Received July 3. Date for Comment, August 1, 1973

Asbestos Manufacturing: No comment
Glass Manufacturing: No comment
Dairy Products Industry: No comment
The Fertilizer & Phosphate Industry: No comment
Rubber Processing Industry: No comment
Inorganic Chemicals Mfg: No comment
Grain Mills: No comment
Phosphate Mfg: No comment
Nonferrous Metals Industry: No comment
Cane Sugar Processing: No comment
Soap & Detergent Mfg: No comment
Meat Packing Industry: No comment
Ferroalloy Industry: No comment
Leather Tanning & Finishing Industry: See enclosure

Very truly yours,

K. Lennart Rost, Chief
Division of Industrial Services
Bureau of Water Quality Control

962

KLR:jig
cc: Mr. Allen Cywin

Martin

COLORADO DEPARTMENT OF PUBLIC HEALTH

4210 EAST 11TH AVENUE • DENVER, COLORADO 80220 • PHONE 388-6111

R. L. CLEERE, M.D., M.P.H., DIRECTOR

July 13, 1973

Environmental Protection Agency
Region VIII
1860 Lincoln Street, Room 900
Denver, Colorado 80203

ATTENTION: Mr. Evan Dildine

RE: Draft Development Document for Effluent Limitations Guidelines and Standards of Performance - Non-Fertilizer Phosphorus Chemicals Industry

Gentlemen:

This Division has no comment on the proposed Guidelines, referenced above.

Very truly yours,

FOR DIRECTOR, WATER QUALITY CONTROL DIVISION

E.B. Pugsley, P.E.
Industrial Waste Consultant

EBP:dls

cc: Mr. Allan Cywin, Director, Effluent Guidelines Division, EPA
Frank Rozich, Water Quality Control Division

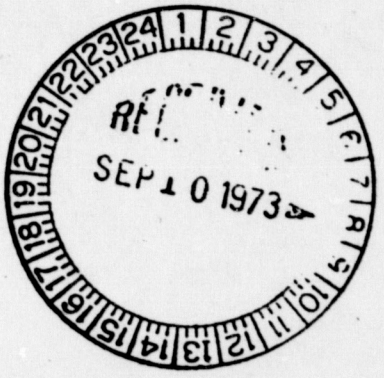
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Mailed

UNITED STATES WATER RESOURCES COUNCIL

SUITE 800 • 2120 L STREET, N.W. WASHINGTON, D.C. 20037

August 30, 1973



Mr. Alvin L. Alm
Assistant Administrator
for Planning and Management
U. S. Environmental Protection Agency
Washington, D. C. 20460

Dear Mr. Alm:

The Water Resources Council has received the Effluent Guidelines regulations for Phosphate Manufacturing and Feedlots prepared pursuant to Sections 304(b) and 306 of the Federal Water Pollution Control Act, and we have no comments to offer at this time. The enclosures with your letter of August 24, 1973, did not include the guidelines for Cement Manufacturing.

Thank you for the opportunity to comment.

Sincerely yours,

P. T. Stuchan

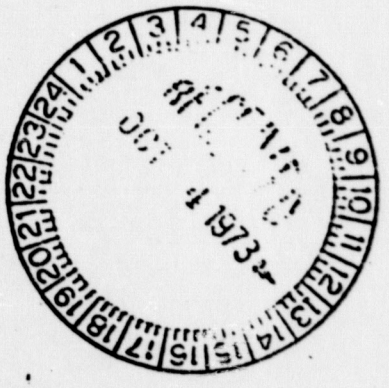
for Gary D. Cobb
Assistant Director

964

MEMBERS: SECRETARIES OF INTERIOR, AGRICULTURE; ARMY, HEALTH, EDUCATION AND WELFARE; TRANSPORTATION, CHAIRMAN, FEDERAL POWER COMMISSION – ASSOCIATE MEMBERS: SECRETARIES OF COMMERCE, HOUSING AND URBAN DEVELOPMENT; ADMINISTRATOR, ENVIRONMENTAL PROTECTION AGENCY – OBSERVERS: DIRECTOR, OFFICE OF MANAGEMENT AND BUDGET; ATTORNEY GENERAL; CHAIRMEN – COUNCIL ON ENVIRONMENTAL QUALITY, RIVER BASIN COMMISSIONS

UNITED STATES WATER RESOURCES COUNCIL
SUITE 800 • 2120 L STREET, N.W. WASHINGTON, D.C. 20037

September 25, 1973



Mr. Alvin L. Alm
Assistant Administrator for
Planning and Management
U. S. Environmental Protection Agency
Washington, D. C. 20460

Dear Mr. Alm:

Water Resources Council staff have reviewed the Economic Analysis of Proposed Effluent Guidelines for the Beet Sugar Industry, EPA-230/1-73-002; Insulation Fiberglass Industry, EPA-230/1-73-011; Industrial Phosphate Industry, EPA-230/1-73-021; Feedlots Industry, EPA-230/1-73-008; and Cement Industry, EPA-230/1-73-004; dated August 1973, and we have no comments to offer.

Thank you for the opportunity to comment.

Sincerely yours,

Gary D. Cobb
Assistant Director

965

MEMBERS: SECRETARIES OF INTERIOR, AGRICULTURE, ARMY, HEALTH, EDUCATION AND WELFARE, THAT ... CHAIRMAN, FEDERAL POWER COMMISSION ... SECRETARIES OF COMMERCE, HOUSING ... DEVELOPMENT, ADMINISTRATOR OF ENVIRONMENTAL PROTECTION AGENCY, CHAIRMAN, COUNCIL ON ENVIRONMENTAL QUALITY AND THE BOARD ... ATTORNEY GENERAL, CHAIRMAN OF ... ON ENVIRONMENTAL QUALITY AND THE BOARD

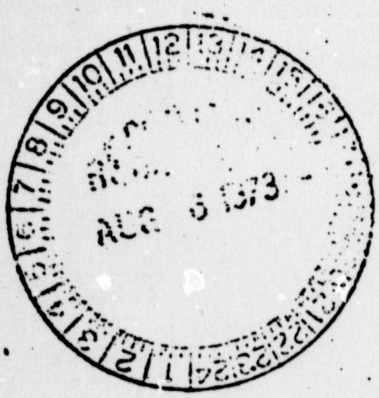
GORDON FULCHER
CHAIRMAN
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J. DOUG TOOLE
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TEXAS WATER QUALITY BOARD

CLAYTON T. GARRISON
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J. E. PEAVY, MD
HUGH C. YANTIS, JR.
EXECUTIVE DIRECTOR

PH. 475-2651
A.C. 512

314 WEST 11TH STREET 78701
P.O. BOX 13246 CAPITOL STATION 78711
AUSTIN, TEXAS



July 31, 1973

RE: Proposed Effluent Guidelines for the Nonfertilizer Phosphorus Chemicals Industry

Mr. Arthur Busch, Regional Administrator
Environmental Protection Agency, Region VI
1600 Patterson, Suite 1100
Dallas, Texas 75201

Dear Mr. Busch:

We have reviewed the draft Development Document for Effluent Limitations Guidelines and Standards of Performance, Non-Fertilizer Phosphorus Chemicals Industry prepared by the General Technologies Corporation, June 1973. This document appears to provide a workable basis for establishing effluent limitations for the nonfertilizer phosphorus chemicals industries. It does appear, however, that the limitations on toxic or hazardous materials may unnecessarily restrict the usage of corrosion inhibitors in industrial cooling waters. The guidelines require that no toxic or hazardous pollutants be added to noncontact cooling waters and boiler waters. We agree that chromium and other materials may pose a significant environmental problem in harmful concentrations. On the other hand, we would recognize that in detectable but very low concentrations, chromium and other hazardous materials would not pose a significant environmental threat.

We also note that the proposed guidelines for noncontact cooling waters would require that the waters discharged not have levels of chromates or other toxic pollutants higher than that of the intake water or the receiving water, whichever is lower. It is conceivable that an intake water with a natural background level of the pollutant would have to be treated to reduce the concentration of that pollutant

to permit the discharge to another body of water which might have a natural lower level of the pollutant. Such a condition may reasonably be expected to occur where the raw water supply happens to be a mineralized groundwater.

It would appear to be appropriate to permit the utilization of these materials to the degree that water quality problems do not result. From a regulatory standpoint, it may be helpful to place a limit on the incremental increase of the pollutant concentration in the water as the water passes through the plant. We appreciate the opportunity to comment on this document.

Sincerely,

Dick Whittington

Dick Whittington, P.E.
Deputy Director

TM:ce

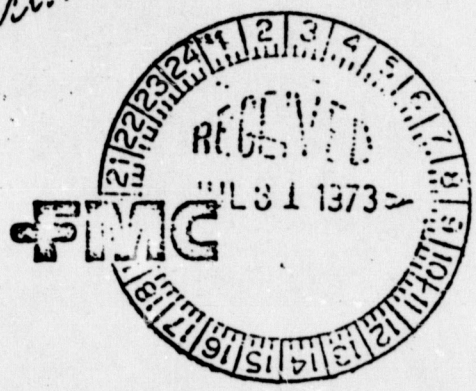
cc: Mr. Allen Cywin, Director
Effluent Guidelines Division
Environmental Protection Agency
Washington, D.C.

FMC Corporation

Chemical Group Headquarters
633 Third Avenue
New York New York 10017
(212) 687 7400

July 27, 1973

Same as MCA Comment Letter



Mr. Allen Cywin
Director, Effluent Guidelines Division
U. S. Environmental Protection Agency
Waterside Mall
Washington, D. C. 20460

Dear Sir:

In reference to the preliminary draft of "Development Document of Effluent Limitations Guidelines and Standards of Performance for the Non-Fertilizer Phosphorus Chemicals Industry", we have the following comments directed to the elemental phosphorus, phosphoric acid, and phosphate producing segments specifically in terms of Level I standards.

Phosphoric Acid and Phosphate Producing Segments

FMC is a major producer of phosphoric acid and various sodium and potassium phosphates at four locations. We agree with the draft in that zero discharge is attainable for a single product plant, e.g. phosphoric acid or sodium tripolyphosphate under special conditions. Indeed, the one FMC plant which produces only one phosphate product has already attained zero discharge by process recycle and the solar evaporation of rainwater runoff since it is located in an area with an average annual rainfall of 6 inches.

The basic recommendation of the draft document is total recycle of all process water and rainwater runoff (Sections IX; 2.0, 3.2.2,3.3). This assumption fails to account for differences in climatic conditions and the physical arrangement of plants which we believe are the most important factors in determining the feasibility of total recycle of rainwater runoff.

At our single product plant it is relatively simple to obtain zero discharge of aqueous wastes simply because of the favorable climatic factors at the location. With an annual rainfall of 6 inches and a resulting net solar evaporation rate for impounded surface waters it becomes simply a matter of collecting rainwater runoff and impounding in evaporation ponds.

At the opposite extreme one of our plants is located in an area with an annual rainfall of 60 inches. Considering this plant has some 17 acres in processing equipment, materials handling areas, loading areas, warehousing, etc., it is not possible to collect this quantity of water for recycle into the process. The draft document (Section VII, 2.6.4) indicates the runoff from the entire plant must be contained.

We believe these two extreme situations within our own company demonstrate the impact of climatic conditions and physical plant arrangement on the feasibility of total recycle of rainwater. We further contend that the draft document in question does not address these factors which raises serious question as to the validity of establishing total recycle of rainwater runoff as a national industrial effluent standard.

Recycle of process water in a multiproduct plant presents several problems involving product contamination. At three of our plants a wide range of products, including various sodium and potassium phosphates, agricultural grade and food grade phosphoric acids are manufactured. Even within the three plants, each with the same product lines, there are wide variations in the manufacturing processes.

In some cases we have continuous production lines producing a single product line throughout the year. At other locations we have production lines which manufacture multiproduct lines by switching the products, including raw materials, as product requirements may dictate. One means for recycling process wastewater in a phosphate plant is as feed water to the phosphorus furnaces. Since the phosphoric acid produced in the furnaces serves both as various grades of merchant acid and as raw materials for various phosphate products, recycle of process wastes to the furnace is limited due to the problem of cross-product contamination.

The second means for recycling process wastewater is as feed to the raw material reaction and drying steps. Cross-contamination again limits recycle particularly when single production units are used for multiproduct lines. The problem is simply that sodium and potassium salts cannot be intermixed or mixed with merchant grade acids including food grade acids.

We recognize that the draft document in question relates specifically to phosphoric acid and sodium tripolyphosphate (STPP). We believe that effluent standards established for these products should be

applicable to plants which only produce these products and not to multiproduct phosphate plants.

In our three multiproduct phosphate plants we have been actively involved in an effluent reduction program. Generally, we have followed the basic concepts in the draft, i.e., separation of the non-contact cooling water and recycle of the process water as much as possible. We have reduced our phosphate effluent levels from 5.4 kg. phosphates (as P) per M kg. of phosphorus consumed to 2.1 kg This program is continuing and we project reaching a 1.0 kg. level upon completion of these projects. The 1.0 kg. level represents an 82% reduction in our phosphate effluent levels. Although there will continue to be a variation in effluent levels between plants, this level could become, we believe, a reasonable basis for a national standard.

Considering the problems of plants located in diverse climatic condi tions, we believe the 1.0 kg. level represents exemplary performance for non-fertilizer multiproduct phosphate plants. Cognizant of the diverse nature of the phosphate industry, we hesitate to recommend any specific effluent level. However, we do consider the 1.0 kg. level to represent a technologically practical limit for the industr

In summary, we feel the draft fails to recognize special climatic and physical plant conditions which have major impacts on the practicability of recycling rainwater runoff in the manufacture of phosphoric acid and STPP. We, therefore, seriously question the establishment of a national standard (Level I) of zero emissions fr these facilities.

We further believe that standards established for these production facilities should not be applicable to multiproduct plants. On thi basis we have proposed an alternative recommendation which we belie can be met using current technology for multiproduct phosphate plan

Elemental Phosphorus Segment

FMC Corporation operates a major elemental phosphorus plant in Pocatello, Idaho. Based on this plant's performance and our review of the draft document, we do not believe there is a single elementa phosphorus plant in the United States which presently meets Level I recommended standards.

The basic recommendation of the draft document is for total recycle of all process water and rainwater runoff (Sections IX; 3.0,3.1.1, 3.1.3).

The justification (Section IX; 3.1.3) for these recommendations is that two plants, TVA and Plant 181, have already achieved zero discharge.

However, Section IX, 3.1.2 of the draft document states in reference to Plant 181, "Under conditions of very abnormally high rainfall which would exceed the capacity of the pond system, the only overflow would be from the final rinse water supply ponds, thereby minimizing the quantities of pollutants even occasionally discharged". We submit that this condition does not meet the criteria for the proposed national effluent standard.

We have contacted TVA and find that in fact process waste streams are discharged both directly and indirectly into the Tennessee River. We, therefore, contend that both plants cited as presently having zero discharge do in fact have discharges. We further believe that this raises serious question as to the validity of establishing zero discharge as a national discharge standard for the elemental phosphorus industry.

We do not wish to propose an alternative Level I standard simply because our experience in elemental phosphorus production is subjected to highly localized conditions which most certainly have an impact on effluent levels. However, we believe the validity of the zero standard has been sufficiently questioned to warrant further study prior to the establishment of a Level I standard.

We wish to take this opportunity to express our appreciation to you for consideration given our comments.

Very truly yours,

Neil C. Elphick

Neil C. Elphick
Director - Environmental Planning

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APPENDIX C

THE FOLLOWING COMMENTS ON NON-FERTILIZER PHOSPHORUS CHEMICAL INDUSTRY SUBMITTED BY FMC CORPORATION

In reference to the preliminary draft of "Development Document of Effluent Limitations Guidelines and Standards of Performance for the Non-Fertilizer Phosphorus Chemicals Industry", we have the following comments directed to the elemental phosphorus, phosphoric acid, and phosphate producing segments specifically in terms of Level I standards.

Phosphoric Acid and Phosphate Producing Segments

FMC is a major producer of phosphoric acid and various sodium and potassium phosphates at four locations. We agree with the draft in that zero discharge is attainable for a single product plant, e.g. phosphoric acid or sodium tripolyphosphate under special conditions. Indeed, the one FMC plant which produces only one phosphate product has already attained zero discharge by process recycle and the solar evaporation of rainwater runoff since it is located in an area with an average annual rainfall of 6 inches.

The basic recommendation of the draft document is total recycle of all process water and rainwater runoff (Sections IX; 2.0, 3.2.2,3.3). This assumption fails to account for differences in climatic conditions and the physical arrangement of plants which we believe are the most important factors in determining the feasibility of total recycle of rainwater runoff.

At our single product plant it is relatively simple to obtain zero discharge of aqueous wastes simply because of the favorable climatic factors at the location. With an annual rainfall of 6 inches and a resulting net solar evaporation rate for impounded surface waters it becomes simply a matter of collecting rainwater and impounding in evaporation ponds.

At the opposite extreme one of our plants is located in an area with an annual rainfall of 60 inches. Considering this plant has some 17 acres in processing equipment, materials handling areas, loading areas, warehousing, etc., it is not possible to collect this quantity of water for recycle into the process. The draft document (Section VII, 2.6.4) indicates the runoff from the entire plant must be contained.

We believe these two extreme situations within our own company demonstrate the impact of climatic conditions and physical plant arrangement on the feasibility of total recycle of rainwater. We further contend that the draft document in question does not address these factors which raises serious question as to the validity of establishing total recycle of rainwater runoff as a national industrial effluent standard.

Recycle of process water in a multiproduct plant presents several problems involving product contamination. At three of our plants a wide range of products, including various sodium and potassium phosphates, agricultural grade and food grade phosphoric acids are manufactured. Even within the three plants,

each with the same product lines, there are wide variations in the manufacturing processes.

In some cases we have continuous production lines producing a single product line throughout the year. At other locations we have production lines which manufacture multiproduct lines by switching the products, including raw materials, as product requirements may dictate. One means for recycling process wastewater in a phosphate plant is as feed water to the phosphorus furnaces. Since the phosphoric acid produced in the furnaces serves both as various grades of merchant acid and as raw materials for various phosphate products, recycle of process wastes to the furnace is limited due to the problem of cross-product contamination.

The second means for recycling process wastewater is as feed to the raw material reaction and drying steps. Cross-contamination again limits recycle particularly when single production units are used for multiproduct lines. The problem is simply that sodium and potassium salts cannot be inter-mixed or mixed with merchant grade acids including food grade acids.

We recognize that the draft document in question relates specifically to phosphoric acid and sodium tripolyphosphate (STPP). We believe that effluent standards established for these products should be applicable to plants which only produce these products and not to multiproduct phosphate plants.

In our three multiproduct phosphate plants we have been actively involved in an effluent reduction program. Generally, we have followed the basic concepts in the draft, i.e., separation of the non-contact cooling water and recycle of the process water as much as possible. We have reduced our phosphate effluent levels from 5.4 kg. phosphates (as P) per M kg. of phosphorus consumed to 2.1 kg. This program is continuing and we project reaching a 1.0 kg. level upon completion of these projects. The 1.0 kg. level represents an 82% reduction in our phosphate effluent levels. Although there will continue to be a variation in effluent levels between plants, this level could become, we believe, a reasonable basis for a national standard.

Considering the problems of plants located in diverse climatic conditions, we believe the 1.0 kg. level represents exemplary performance for non-fertilizer multiproduct phosphate plants. Cognizant of the diverse nature of the phosphate industry, we hesitate to recommend any specific effluent level. However, we do consider the 1.0 kg. level to represent a technologically practical limit for the industry.

In summary, we feel the draft fails to recognize special climatic and physical plant conditions which have major impacts on the practicability of recycling rainwater runoff in the manufacture of phosphoric acid and STPP. We, therefore, seriously question the establishment of a national standard (Level I) of zero emissions from these facilities.

We further believe that standards established for these production facilities should not be applicable to multiproduct plants. On this basis we have proposed an alternate recommendation which we believe can be met using current technology for multiproduct phosphate plants.

ELEMENTAL PHOSPHORUS SEGMENT

FMC Corporation operates a major elemental phosphorus plant in Pocatello, Idaho. Based on this plants performance and our review of the draft document, we do not believe there is a single elemental phosphorus plant in the United States which presently meets Level I recommended standards.

The basic recommendation of the draft document are for total recycle of all process water and rainwater runoff (Section IX, 3.0.3.1.1, & Section IX, 3.1.3). The justification for these recommendations is that two plants, TVA and Plant 181, have already achieved zero discharge.

However, Section IX, 3.1.2 of the draft document states in reference to Plant 181, "under conditions of very abnormally - high rainfall which would exceed the capacity of the pond system, the only overflow would be from the final rinse water supply ponds, thereby minimizing the quantities of pollutants even occasionally discharged." We submit that this condition does not meet the criteria for the proposed National effluent standard.

We have contacted TVA and find that, in fact, process waste streams are discharged both directly and indirectly into the Tennessee River. We, therefore, contend that both plants cited as presently having zero discharge do, in fact, have discharges. We further believe this raises serious question as to the validity of establishing zero discharge as a National discharge standard for the elemental phosphorus industry.

We do not wish to propose an alternative Level I standard simply because our experience in elemental phosphorus production is subjected to highly localized conditions which most certainly have an impact on effluent levels. However, we believe the validity of the zero standard has been sufficiently questioned to warrant further study prior to the establishment of a Level I standard.

ENVIRONMENTAL PROTECTION AGENCY

EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS OF PERFORMANCE FOR NEW SOURCES

Advance Notice of Public Review Procedures

Advance notice is hereby given concerning notices of proposed rule making to be published by the Environmental Protection Agency ("EPA") with respect to effluent limitations guidelines, standards of performance, and pretreatment standards for new sources pursuant to sections 304(b) 306 and 307(c) of the Federal Water Pollution Control Act, as amended (33 U.S.C. 1251, 1314, 1316 and 1317(c); 86 Stat. 816 et seq.; Pub. L. 92-500) ("the Act"). The purpose of this notice is to facilitate public comment upon the regulations to be promulgated under sections 304(b), 306 and 307(c), both before and after the publication of the notices of proposed rule making. In addition, this notice will explain EPA's overall plans for development of effluent limitations guidelines and standards of performance for new sources and the approach which is being taken by the Agency in discharging the duties placed upon the Administrator under sections 304(b), 306 and 307(c) of the Act.

EPA believes that the exposure of the technical basis and reasoning underlying regulations to be established pursuant to sections 304(b), 306 and 307(c) is essential to the promulgation of sound effluent limitations guidelines and standards of performance for new sources. At the same time, because of the deadlines for action imposed upon the Administrator under the Act, both EPA and the public will be pressed to analyze and resolve highly complex and important issues in a relatively short time. In order both to develop sound regulations and meet the time schedules set by the Act, EPA intends to identify as many issues and elicit points of criticism at the earliest possible time. To resolve such issues often will require further staff work and management decision-making within EPA and may necessitate substantial redrafting of regulations and support documents. Therefore, extensive external review cannot be postponed until internal EPA review of initial recommendations for effluent limitations guidelines and standards of performance has been completed, but must proceed concurrently with EPA's own internal review and decision-making if the Act's deadlines are to be met.

EPA has already begun this process by seeking comments upon draft technical reports from persons and organizations known to be interested in particular source categories. These reports (which are discussed further below) contain tentative recommended effluent limitations guidelines and standards of performance. This notice seeks to supplement this already initiated external review and facilitate further review and public comment in late August and early September, when notices of proposed rule making will be published in the FEDERAL REGISTER. The notice is divided into three parts. First, the basic legal authority for regulations concerning effluent limitations guidelines and standards of performance for new sources will be set forth. Second, EPA's general methodology will be described. Third, the means by which EPA has to date, and will in the future, seek the widest possible public scrutiny of the technical and legal basis for the regulations to be established will be explained.

I. *Legal authorities.*—(a) *Existing point sources.* Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which require the application of the best practicable control technology currently available as defined by the Administrator pursuant to section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which require the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to section 304(b) of the Act.

Section 304(b) of the Act requires the Administrator to publish regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available (the 1977 requirement) and the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operating methods and other alternatives (the 1983 requirement).

(b) *New sources.* Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants.

Section 306(b)(1)(B) of the Act requires the Administrator to propose regulations establishing Federal standards of performance for categories of new sources included in a list published pursuant to section 306(b)(1)(A) of the Act. The Administrator published in the FEDERAL REGISTER of January 16, 1973, (38 FR 1821) a list of source categories for which standards of performance for new sources will initially be established. Section 306(a)(2) defines "new source" as "any source, the construction of which is commenced after the publication of proposed regulations prescribing a stand-

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ard of performance under this section which will be applicable to such source • • •."

Section 307(c) of the Act requires the Administrator to promulgate pretreatment standards for a category of new sources at the same time that standards of performance for that category are promulgated pursuant to section 306. EPA presently plans to include in proposed and promulgated regulations establishing standards of performance for new sources, provisions which will require application of pretreatment standards which are consistent with EPA's proposed pretreatment standards for existing sources. The basis for the latter standards is set forth in the FEDERAL REGISTER of July 19, 1973 (38 FR 19236) under 40 CFR Part 128. The provisions and rationale of Part 128 are equally applicable to sources which would constitute "new sources", under section 306 if they were to discharge pollutants directly to navigable waters, except for § 128.133. That section provides a pretreatment standard for "incompatible pollutants" which requires application of the "best practicable control technology currently available," subject to an adjustment for amounts of pollutants removed by the publicly owned treatment works. Since the pretreatment standards to be promulgated under section 307(c) apply to new sources, the regulations establishing standards of performance for new sources will amend § 128.133 to require application of the standard of performance for new sources rather than the "best practicable" standard applicable to existing sources under sections 301 and 304(b) of the Act.

2. *EPA's methodology*—(a) *Overall approach.* The technical studies discussed below and the development of regulations for effluent limitations guidelines and standards of performance are undertaken in the following manner. The point source category is first studied for the purpose of determining whether separate limitations and standards are appropriate for different segments within the category. This analysis includes a determination of whether differences in raw material used, product produced, manufacturing process employed, age and size of plants, waste water constituents and other factors require development of separate limitations and standards for different segments of the point source category. The raw waste characteristics for each such segment are then identified. This includes an analysis of (1) the source, flow and volume of water used in the process employed and the sources of waste and waste waters in the plant; and (2) the constituents of waste waters. The constituents of the waste waters which should be subject to effluent limitations guidelines and standards of performance are then identified.

Next, the control and treatment technologies existing within each segment are identified. This includes an identification of each distinct control and treatment technology, including both in-plant and end-of-process technologies, which exists or is capable of being designed for each segment. It also includes an identification of the effluent level resulting from the application of each of the treatment and control technologies, in terms of the amount of constituents and the chemical, physical, and biological characteristics of pollutants. The problems, limitations and reliability of each treatment and control technology are also identified. In addition, any non-water quality environmental impact, such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, noise and radiation is examined. Finally, the energy requirements of each control and treatment technology are determined, as well as the cost of the application of such technologies.

This information is then evaluated in order to determine what levels of technology constitute the "best practicable control technology currently available", "best available technology economically achievable" and the "best available demonstrated control technology, processes, operating methods, or other alternatives." In identifying such technologies, various factors are considered including the total cost of the application of technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the process employed, the engineering aspects of the application of various types of control techniques, process changes and non-water quality environmental impact (including energy requirements).

The data on which the above analysis was performed included EPA permit applications, EPA sampling and inspections, industry submissions and consultant reports, including the reports discussed below.

(b) *Technical studies.* Studies of some thirty point source categories for which regulations will initially be promulgated were instituted by EPA as soon as possible after passage of the Federal Water Pollution Control Act Amendments of 1972 (October 18, 1972). These studies constitute in-depth analyses of the technological feasibility and economic costs of reducing or eliminating discharges of pollutants. The studies, along with other information obtained by EPA in the course of internal and external review of the resulting reports or otherwise available to EPA, will serve as a foundation for the regulations to be issued under sections 304(b) and 306 of the Act.

To have attempted to amass within the Agency in a very short period of time the large number of technical personnel with experience in the many diverse point source categories to be covered would have been impractical. Therefore, the overall data base and initial analysis have been obtained through contracts with qualified technical consultants. These consultants were instructed to perform in-depth studies of each point source category, under the supervision and with the assistance of EPA, in accordance with the methodology described above. The resulting draft reports include initial tentative recommendations with respect to the effluent limitations guidelines and standards of performance for the particular point source category concerned. The draft reports and recommendations are then subjected to extensive internal and external review. The contractors are assisting in the initial collection and collation of the data base. The responsibility for establishing effluent limitations guidelines and standards of performance for new sources, of course, remains with EPA.

For each of the point source categories covered by the technical studies, EPA is also conducting supplementary studies of the economic impact which could result from application of alternative control and treatment technologies. These studies add to the economic analyses already undertaken as part of the technical studies, which center upon the investment and operating costs associated with various alternative control and treatment technologies, by estimating the broader economic effects which might result from the required application of various technologies. The economic impact studies will investigate effects of alternative approaches in terms of product price increases, effects upon employment and the continued viability of affected plants, effects upon foreign trade and other competitive effects. These reports may be published in the same manner as the EPA draft reports, as discussed in section 3(c) below.

Contractors' technical studies of the following point source categories have been completed:

1. Pulp, Paper and Paperboard Mills
2. Builders Paper and Board Mills
3. Meat Product and Rendering Processing
4. Dairy Product Processing
5. Grain Mills
6. Canned and Preserved Fruits and Vegetables Processing
7. Canned and Preserved Seafood Processing
8. Beet Sugar Processing
9. Cane Sugar Processing
10. Textile Mills
11. Cement Manufacturing
12. Feedlots
13. Electroplating
14. Organic Chemicals Manufacturing
15. Inorganic Chemicals Manufacturing
16. Plastics and Synthetic Materials Manufacturing
17. Soap and Detergent Manufacturing
18. Fertilizer Manufacturing
19. Petroleum Refining
20. Iron and Steel Manufacturing
21. Nonferrous Metals Manufacturing
22. Phosphate Manufacturing
23. Steam Electric Powerplants
24. Ferroalloy Manufacturing
25. Leather Tanning and Finishing
26. Glass Manufacturing
27. Insulation Fiberglass Manufacturing
28. Timber Products Processing
29. Beet Sugar Processing Industry
30. Insulation Fiberglass Industry

3. *Public participation in the development of regulations*—(a) *Review of the draft contractors' reports.* The completed contractors' reports are presently undergoing intensive analysis within

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EPA and are also receiving extensive external review and comment. This process of internal and external review is being carried on simultaneously in order to make the most of the time available under the Act. Once the contractors' draft reports are received by EPA, they are immediately distributed to a list of external reviewers for critical analysis. The persons or institutions listed below have been sent the draft reports. They have been asked to comment within 30 days so there will be time for their comments to be taken into account by EPA when preparing proposed rule making documents.

STATES

Alabama Water Improvement Commission
State Office Building
Montgomery, Alabama 36104

State of Alaska
Department of Environmental Conservation
Pouch O
Juneau, Alaska 99801

Commission of Arizona State Department of Health
4019 N. 33rd Avenue
Phoenix, Arizona 85017

Department of Pollution Control and Ecology
1100 Harrington Avenue
Little Rock, Arkansas 72202

California State Water Resources Control Board
Sacramento, California 95814

Water Pollution Control Division
Colorado Department of Health
4210 E 11th Avenue
Denver, Colorado 80220

Division of Water Compliance and Hazardous Substances
Department of Environmental Protection
State Office Building
Hartford, Connecticut 06115

Department of Natural Resources and Environmental Control
Capitol Complex
Tatnall Building
Dover, Delaware 19901

Department of Pollution Control
2562 Executive Center Circle East
Tallahassee, Florida 32301

Environmental Protection Division
Department of Natural Resources
47 Trinity Avenue, S.W.
Atlanta, Georgia 30334

Assistant Director for Environmental Health
Hawaii State Department of Health
P.O. Box 3378
Honolulu, Hawaii 96801

Indiana Stream Pollution Control Board
1330 West Michigan Street
Indianapolis, Indiana 46206

State of Idaho
Department of Environmental and Community Services
State House
Boise, Idaho 83720

Water Quality Management Division
Department of Environmental Quality
Lucas State Office Building
Des Moines, Iowa 50319

Division of Environmental Health
Kansas State Department of Health
535 Kansas Avenue
Topeka, Kansas 66603

Kentucky Water Pollution Control Commission
275 East Main Street
Frankfort, Kentucky 40601

Louisiana Stream Control Commission
P.O. Drawer FC
University Station
Baton Rouge, Louisiana 70803

Environmental Health Division
Louisiana State Board of Health
New Orleans, Louisiana

Department of Environmental Protection
State House
Augusta, Maine 04430

Water Resources Administration
Tower State Office Building
D2 Water Resources
Annapolis, Maryland 21401

Division of Water Pollution Control
State Office Building
100 Cambridge Street
Boston, Massachusetts 02202

Michigan Water Resources Commission
Steven T. Mason Building
Lansing, Michigan 48916

Minnesota Pollution Control Agency
State Board of Health Building
717 Delaware Street, SE
Minneapolis, Minnesota 55440

Mississippi Air and Water Pollution Control Commission
P.O. Box 827
Jackson, Mississippi 39205

Missouri Clean Water Commission
P.O. Box 154
Jefferson City, Missouri 65101

Division of Environmental Sanitation
State Department of Health
Cogswell Building
Helena, Montana 59601

Department of Environmental Control
1420 P Street
Lincoln, Nebraska 68509

Nevada Commission of Environmental Protection
201 South Fall Street
Carson City, Nevada 89701

New Hampshire Water Supply and Pollution Control Commission
Prescott Park
105 Loudon Road
Concord, New Hampshire 03301

Department of Environmental Protection
P.O. Box 1390
Trenton, New Jersey 08625

New Mexico Environment Improvement Agency
P.O. Box 2348
Santa Fe, New Mexico 87501

Industrial Waste Bureau
New York State Department of Environmental Conservation
50 Wolf Road
Albany, New York 12201

Office of Air and Water Resources
Department of Natural and Economic Resources
P.O. Box 27687
Raleigh, North Carolina 27611

Environmental Health and Engineering Services
Department of Health
State Capitol
Bismarck, North Dakota 58501

Ohio Environmental Protection Agency
Columbus, Ohio 43216

Department of Pollution Control
2241 N.W. 40th Street
Oklahoma City, Oklahoma 73112

Oregon Department of Environmental Quality
1234 S.W. Morrison
Portland, Oregon 97205

Bureau of Sanitary Engineering
Department of Environmental Resources
P.O. Box 2351
Harrisburg, Pennsylvania 17120

Division of Water Pollution Control
Rhode Island Department of Health
State Office Building
Providence, Rhode Island 02903

South Carolina Pollution Control Authority
P.O. Box 11628
Columbia, South Carolina 29211

Division of Sanitary Engineers and Environmental Protection
State Department of Health
State Capitol
Pierre, South Dakota 57501

Division of Water Quality Control
Department of Public Health
621 Cordell Hull Building
Nashville, Tennessee 37219

Texas Water Control Board
P.O. Box 13246
Capitol Station
Austin, Texas 78711

Bureau of Environmental Health
Division of Health
44 Medical Drive
Salt Lake City, Utah 84113

Vermont Agency of Environmental Conservation
Montpelier, Vermont 05302

Virginia State Water Control Board
1010 State Office Building
Richmond, Virginia 23219

Washington Department of Ecology
P.O. Box 829
Olympia, Washington 98504

West Virginia Division of Water Resources
Department of Natural Resources
1201 Greenbriar Street
Charleston, West Virginia 25311

Division of Environmental Protection
Wisconsin Department of Natural Resources
P.O. Box 450
Madison, Wisconsin 53701

Sanitary Engineering Services
Division of Health and Medical Services
Department of Health and Social Services
State Office Building
Cheyenne, Wyoming 82001

TERRITORIES

Environmental Quality Commission
Government of Samoa
Pago-Pago, Tutuila
American Samoa 96920

Water Pollution Control Program
Government of Guam
P.O. Box 2816
Agana, Guam 96910

Environmental Quality Board
P.O. Box 11785
San Juan, Puerto Rico 00910

Office of High Commission
Division of Environmental Health
Trust Territory of the Pacific Islands
Saipan, Mariana Island 96950

RIVER BASIN COMMISSIONS

Delaware River Basin Commission
25 State Police Drive
West Trenton, New Jersey 08628

New England Interstate Water Pollution Control Commission

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607 Boylston Street
Boston, Massachusetts 02116
Ohio River Valley Sanitation Commission
414 Walnut Street
Cincinnati, Ohio 45202

The reports have also been transmitted to the following agencies or organizations:

AGENCIES AND OFFICES OF/OR RELATED TO THE FEDERAL GOVERNMENT

Department of Agriculture
Atomic Energy Commission
Department of Commerce
Department of Defense
Federal Power Commission
Department of Health, Education, and Welfare
Department of Housing and Urban Development
Department of the Interior
Office of the Energy Advisor
Department of the Treasury
National Industrial Pollution Control Council
U.S. Department of Commerce
Water Resources Council
Tennessee Valley Authority

PUBLIC INTEREST GROUPS

The American Society of Civil Engineers
The American Society of Mechanical Engineers
Businessmen for the Public Interest
Conservation Division
National Wildlife Federation
The Conservation Foundation
Environmental Defense Fund, Inc.
Hudson River
Sloop Restoration, Inc.
Natural Resources Defense Council
Water Pollution Control Federation

INDUSTRY TRADE ASSOCIATIONS OR COMPANIES

The Aluminum Association
Aluminum Smelting and Recycling Institute
American Corn Millers Federation
American Electroplaters' Society
American-Florida Sugar Cane League
American Frozen Food Institute
American Hardboard Association
American Iron and Steel Institute
American Livestock Feeders Association
American Meat Institute
American Mining Congress
American National Cattleman's Association
American Paper Institute
American Petroleum Institute
American Plywood Association
American Public Power Association
American Shrimp Canners Association
American Wood Preservers Association
American Wood Preservers Institute
American Textile Manufacturers Institute
A.S.G. Industries, Inc.
Atomic Industrial Forum, Inc.
Beet Sugar Development Foundation
Carpet and Rug Institute
Catfish Farmers of America
Chesapeake Bay Seafood Industries Association, Inc.
Chlorine Institute
Copper and Brass Fabricators Council
Corn Refiners Association, Inc.
Dairy Industry Committee
Dimmitt Agricultural Industry
Edison Electric Institute
Environmental Pollution Control Program
Glass Container, Inc.
The Ferroalloy Association
The Fertilizer Institute
Ford Motor Company
Glass Division
Glass Containers Manufacturers Institute
Hawaiian Sugar Planters Association
Hardwood Plywood Manufacturing Association
Institute of American Poultry Industries
International Institute of Synthetic Rubber Producers
Libbey-Owens-Ford Co.
Manufacturing Chemists Association
Metal Finishers Supplier's Association
Millers' National Federation
National Association of Electric Companies
National Association of Metal Finishers
National Broiler Council
National Canners Association
National Council of the Paper Industry for Air and Stream Improvement, Inc.
National Independent Meat Packers Association
National Fisheries Association
National Forest Products Association
National Milk Producers Federation
National Pork Producers Association
National Tanners Association, Inc.
National Rural Electric Cooperative Association
Northern Textile Association
National Soft Wheat Millers Association
Portland Cement Association
P.P.G. Industries, Inc.
Protein Cereal Products Institute
Puerto Rico Land Administration
Rice Millers Association
Rubber Manufacturing Association
Technical Association of the Pulp and Paper Industry
Soap and Detergent Association
Synthetic Organic Chemical Manufacturers Association
Tanners Council of America, Inc.
Tennessee Valley Public Power Association
Tuna Research Foundation, Inc.
Technical Association of the Pulp and Paper Industry
United States Beet Sugar Association
United States Cane Sugar Refiner's Association
Western States Meat Packers Association
Western Wood Preserver Association

(b) *Public availability of draft technical reports.* The draft reports are voluminous and rapid reproduction in large quantities is difficult to accomplish. In order to maximize the usefulness of early external review of the reports, the reports must be transmitted to interested persons immediately upon receipt by EPA. Printing of substantial quantities of the reports would consume two to three weeks and, under applicable federal regulations, no more than approximately 160 copies of the reports may be provided through outside printing contracts. The 160 copies of the report supplied by the contractors have already been largely exhausted in transmissions to the organizations listed above, and for internal review purposes within EPA. However, a copy of every report is available in each of EPA's regional offices, which are listed in the Appendix to this notice, and a complete set of the reports is also available in EPA's Washington offices (Office of Public Affairs, Environmental Protection Agency, Room W-327, Waterside Mall, Washington, D.C. 20460). The Washington Office will also maintain a complete set of comments received from the public upon draft reports and upon the notices of proposed rule making which will subsequently be published. The draft reports, revised EPA reports which are described below, and all public comments, will be available for inspection and copying during regular business hours. Under EPA's information regulations (40 CFR, Part 2), a fee may be required for making copies.

In addition to review of the EPA copies of the reports, interested persons may in many instances obtain a copy of a draft report by contacting an organization listed above with which they have an affiliation or by seeking to review a copy in the possession of the appropriate State agency.

(c) *Public availability of EPA draft reports.* Upon conclusion of internal and external review of the initial draft reports and their tentative recommendations, an EPA draft report will be prepared in support of proposed regulations to be issued in the FEDERAL REGISTER. The EPA draft report will be published simultaneously with the notice of proposed rule making. The EPA draft report may be different from the contractors' reports, particularly as to the assessment of practicability or availability of technology, and the conclusions reached with respect to effluent limitations guidelines and standards of performance for new sources.

However, EPA does not anticipate that the EPA report will be markedly different in terms of the fundamental data base for the regulations. In most cases, major issues or objections to the approach taken or the conclusions reached in the EPA draft report will have already been raised by the contractors' draft report. Criticisms of the adequacy of the data base and the analytical methods employed should therefore be expressed now rather than after the notice of proposed rule making.

Nevertheless, EPA does not regard the contractors' draft report as an official EPA document and additional comments will, of course, be solicited once the EPA draft report and the associated proposed regulations are published. (A final EPA report will also be prepared and published in support of the final regulations promulgated under sections 301, 304(b), 306 and 307(c)). The EPA draft report will be sent to the list of reviewers set forth earlier in this notice. In addition, EPA is establishing a mailing list of other persons wishing to obtain a copy of the EPA draft report. Any person wishing to be included on the list should so request as soon as possible, but no later than August 20, 1973. The request should be addressed to the "EPA Information Center, Attention: Mr. Philip B. Wisman, Environmental Protection Agency, Room W-327, Waterside Mall, Washington, D.C. 20460", and should indicate which specific reports the person or organization is interested in receiving. EPA will transmit a copy of the EPA draft report to those on the mailing list, as soon as the report is available. Copies of the EPA draft reports will otherwise be transmitted, upon request to EPA, at the address just quoted, as soon as possible. The economic studies referred to in section 2(b) above will be made available upon request in the same manner as the EPA draft reports.

EPA desires to make copies of all reports available to interested parties wishing to comment as soon as possible. EPA therefore requests the cooperation of the

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public who are interested in, but not directly affected by, the proposed regulations in awaiting the final EPA report to be published after the final regulation is printed in the FEDERAL REGISTER, rather than requesting copies of the EPA draft reports.

(d) *Solicitation of public comments.* By seeking comments upon the initial draft reports which have already been prepared, and the initial recommended guidelines and standards which those reports contain, much of the analysis and comment which would ordinarily occur after notices of proposed rule making are published is taking place now. In this way the resolution of many issues can be accomplished even before notices of proposed rule making are published. These issues will be identified and their resolution explained in the notices of proposed rule making. Issues which remain unresolved will be highlighted in the notices. In addition, EPA hopes to enable all interested parties to be sufficiently familiar with the complex technical details underlying the proposed effluent limitations and standards so that they can respond to notices of proposed rule making in a relatively short time. In order to meet the deadlines imposed by the Act, the present plan is that the notices of proposed rule making will request formal public comments within 21 days of publication of the notices in the FEDERAL REGISTER. Those persons who have indicated their desire to be included on the mailing list described above will receive copies of EPA's draft report supporting the proposed regulations in the FEDERAL REGISTER. As noted, these reports will reflect EPA's judgment as to the proper regulations; however, they will be based in large part upon the initial draft reports (which will have been available in most cases since early July 1973) and any comments received thereon.

EPA will consider all comments received up to the time indicated in the notices of proposed rule making. In addition, to the extent time allows, early comments upon the initial draft reports will be considered when developing proposed rule making regulations.

(e) *Conclusion.* In summary, EPA is, by this notice, seeking to encourage as wide ranging and thorough public review prior to proposal and promulgation of effluent limitations guidelines and standards of performance as is possible within the time allowed. The following specific steps may be taken by interested persons:

1. Submit comments upon initial draft reports and economic studies. To facilitate rapid transmission of comments to the persons concerned within EPA, and also have a copy which is immediately available for public review, EPA requests that comments be submitted in triplicate. All comments received before or after publication of the notice of proposed rule making, as well as all technical and economic reports, will be available for inspection and copying at the Office of Public Affairs, Room 727, West Tower, Waterside Mall, during regular business hours (8:00 a.m.–4:30 p.m.).

2. Request inclusion on a mailing list for the EPA draft reports and economic studies which will be published about the same time as notices of proposed rule making in the FEDERAL REGISTER. Requests to be included on the mailing list should be received by August 20, 1973 and should indicate which specific reports are requested.

3. Comment upon the notices of proposed rule making and the associated draft EPA technical and economic reports. All comments received within 21 days after publication of the notices in the FEDERAL REGISTER will be considered.

4. All public comments, requests to be included on the mailing list for reports and other requests for reports may be addressed to "EPA Information Center, Attention: Mr. Philip B. Wiseman, Environmental Protection Agency, Room W-327, Waterside Mall, Washington, D.C. 20460."

In conclusion, it should be emphasized that EPA seeks comments upon its overall approach and legal interpretation of its responsibilities under sections 304(b), 306 and 307(c) of the Act, as well as upon the technical aspects of the initial draft reports, and the EPA reports to be issued. However, it should be also emphasized that the early expression of comments is essential if EPA is to be able to make whatever adjustments and responses which may be necessary in time to satisfy its responsibilities under the Act. In the event comments are in the nature of criticisms as to the adequacy of data which is available or which may be relied upon by the Agency, comments should identify any additional data which may be available and should indicate how such data is pertinent to the development of regulations under sections 301, 304(b), 306 and 307(c) of the Act. In the event comments address the approach taken to establishing an effluent limitation guideline or standard of performance, EPA solicits suggestions as to what alternative approach should be taken, or result reached, and why and how this fits with the detailed requirements of sections 304(b), 306 and 307(c) of the Act.

Dated: July 31, 1973.

ROBERT L. SANSOM,
Assistant Administrator for Air and Water Programs.

APPENDIX

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[FR Doc.73-16133 Filed 8-3-73;8:45 am]

FEDERAL COMMUNICATIONS COMMISSION

[Report 659]

COMMON CARRIER SERVICES INFORMATION [1]

Domestic Public Radio Services Applications Accepted for Filing [2]

JULY 30, 1973.

Pursuant to §§ 1.227(b)(3) and 21.30 (b) of the Commission's rules, an application, in order to be considered with any domestic public radio services application appearing on the attached list, must be substantially complete and tendered for filing by whichever date is earlier: (a) The close of business one business day preceding the day on which the Commission takes action on the previously filed application; or (b) Within 60 days after the date of the public notice listing the first prior filed application (with which subsequent applications are in conflict) as having been accepted for filing. An application which is subsequently amended by a major change will be con-

[1] All applications listed in the appendix are subject to further consideration and review and may be returned and/or dismissed if not found to be in accordance with the Commission's rules, regulations and other requirements.

[2] The above alternative cut-off rules apply to those applications listed in the appendix as having been accepted in Domestic Public Land Mobile Radio, Rural Radio, Point-to-Point Microwave Radio and Local Television Transmission Services (Part 21 of the rules).

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EPA 440/1-73/006

Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the

PHOSPHORUS DERIVED CHEMICALS

Segment of the Phosphate Manufacturing Point Source Cataegory



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

AUGUST 1973

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Publication Notice

This is a development document for proposed effluent limitations guidelines and new source performance standards. As such, this report is subject to changes resulting from comments received furing the period of public comments of the proposed regulations. This document in its final form will be published at the time the regulations for this industry are promulgated.

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DEVELOPMENT DOCUMENT

for

PROPOSED EFFLUENT LIMITATIONS GUIDELINES

and

NEW SOURCE PERFORMANCE STANDARDS

for the

PHOSPHORUS DERIVED CHEMICALS SEGMENT OF THE PHOSPHATE MANUFACTURING

POINT SOURCE CATEGORY

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ABSTRACT

A study was made of the phosphate manufacturing point source category by the General Technologies Corporation for the Environmental Protection Agency, for the purpose of developing effluent limitation guidelines, Federal standards of performance, and pretreatment standards for the industry, to implement Sections 304, 306 and 307 of the Federal Water Pollution Control Act Amendments of 1972.

For the purpose of this study, the phosphate manufacturing industry was defined as the manufacture of the following chemicals: phorphorus (and by-product ferrophosphorus), phosphoric acid (dry process only), phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, phosphorus oxychloride, sodium tripolyphosphate and the calcium phosphates.

Effluent limitation guidelines were developed as a result of this study, defining the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the best available technology economically achievable which must be achieved by existing point sources by July 1, 1977 and July 1, 1983, respectively.

The standards of performance for new sources, were also defined.

Except for PCl_3 and $POCl_3$ manufacture, the recommended best practicable control technologycurrently available for the entire industry is no discharge of process waste water pollutants to navigable waters. The quantitative limitations upon each type of pollution parameter permitted for PCl_3 and $POCl_3$ manufacturing discharges were defined; they are basically the remaining constituents after waste water neutralization and removal of suspended solids. No harmful materials may be discharged.

Application of the best available technology economically achievable and best demonstrated technology for treating dissolved solids would enable the PCl_3 and $POCl_3$ manufacturing operations to achieve no discharge of waste water pollutants.

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SECTION I

CONCLUSIONS

For the purpose of establishing effluent limitations guidelines and standards of performance, the phosphate manufacturing point source category was divided into the phosphorus production, the phosphorus consuming subcategory, and the phosphates subcategories.

Phosphorus and phosphoric acid production were included in this study because they are necessary prequesites to phosphate synthesis. It is also appropriate from technical standpoints to include these chemicals in this study rather than in the inorganic chemical point source category. Other phosphorus consuming chemicals such as PCl_3 and P_2O_5 were included for the same reasons. Processes solely concerned with phosphates to be used as fertilizers are studied under the fertilizer point source category.

The phosphorus-production subcategory of the industry is characterized by large quantities of raw process wastes, including highly deleterious phossy water and highly-acidic scrubber and quenching waste waters, both containing large quantities of fluorides, other dissolved solids, and suspended solids. Through a combination of in-process controls and end-of- process treatment, several plants within this segment have achieved zero discharge of phossy water, two have achieved zero discharge of other process waste waters, and one has achieved zero discharge of any waste water. While other plants now demonstrate abatement practices resulting in 97 percent or greater reduction in the raw waste load before discharge, the total recycle of process water without any discharge has been aptly demonstrated using the best practicable control technology.

The phorphorus-consuming subcategory of the industry is characterized by the absence of direct process waste water; the chemicals produced are readily hydrolyzed so that the processes are essentially dry. However, just because the products are readily hydrolyzed, water is universally used for air pollution abatement scrubbing of tail gases, for periodic cleaning of reaction vessels, and for the general washing of shipped containers; all resulting in acidic waste waters. In addition, water is used in protecting and transferring the raw material, elemental phosphorus, and phossy water is therefore a raw waste from this segment. Except for the manufacture of dry-process phosphoric acid (where in-process control has been demonstrated to achieve zero discharge of aqueous wastes), this segment has not yet achieved sufficient reduction of effluents. The application, however, of currently-available technology is shown by this study to permit total recycle of waste waters (and so zero discharge) for the manufacture of P_2O_5 and P_2S_5; and to achieve the neutralization and removal of most suspended solids prior

to discharge for the manufacture of PCl_3 and $POCl_3$. For these latter two processes, more expensive but still economically achievable technologies are available for treating the chlorides so as to achieve zero discharge.

The phosphates segment of the industry, i.e., the group of chemicals manufactured from phosphoric acid, is characterized by acids and by finely-divided solids in the raw aqueous wastes. Several plants have already achieved zero discharge by in- process controls and by end-of-process treatment; and this study shows how the entire segment may achieve zero discharge by applying currently available practicable technology.

The general conclusion reached is that the industry has already solved its most serious raw waste problem, that is, the abatement of water pollution from phosphorus-producing facilities; and that the very high-volume manufacturing processes (phosphorus, phosphoric acid, sodium tripolyphosphate, and feed-grade calcium phosphate) have already achieved zero discharge. The remainder of the industry, made up of much smaller-volume plants, has lagged behind in effluent reduction, but technology is available to make the entire industry notable.

SECTION II

RECOMMENDATIONS

The recommended effluent limitations quidelines based upon best practicable control technclogy currently available is no discharqe of process waste water pollutants to naviqable waters for the manufacture of the following chemicals:

Phosphorus Production Cateqory
Phosphorus (and Ferrophosphorus)
Phosphorus Consuminq Subcateqory
Phosphoric Acid (Dry Process)
Phosphorus Pentoxide
Phosphorus Pentasulfide
Phosphate Production Subcateqory
Sodium Tripolyphosphate
Calcium Phosphates (Food Grade)
Calcium Phosphates (Animal Feed Grade)

The recommended effluent limitations for this technoloqy for phosphorous trichloride and phosphorous oxychloride of the phosphorus consuminq subcateqory are qiven in Table 1.

Table 1. Recommended Best Practicable Control Technoloqy Currently Available for the Manufacture of Phosphorus Trichloride and Phosphorus Oxychloride. (Process Water)

The recommended effluent limitations quidelines based upon best practicable control technoloqy currently available for process water for the manufacture of PCl_3 and $POCl_3$ are:

	maximum 30 day averaqe	
	Phosphorus Trichloride	Phosphorus Oxychloride
Total Suspended Solids: kg/kkq	0.7	0.15
(lb/ton)	(1.4)	(0.3)
Total Dissolved Solids: kg/kkq	5	3.5
(lb/ton)	(10)	(7)
pH	6.0-9.0	6.0-9.0

The above guidelines apply to the maximum averaqe of daily values for any period of 30 consecutive days. The maximum for for any one day for of total suspended solids and total dissolved solids are twice the consecutive 30 day averaqe value. The pH limitation must be met at all times. It is recommended that noncontact cooling water allowed to be

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discharged. Effluent limitations for this waste stream are expected to be covered in future studies. For the purposes of this report, process water is defined as any water that comes into direct contact with any raw material, intermediate, product, by-product or gas or liquid that has accumulated such constituents.

The recommended effluent limitations guidelines based upon best available technology economically achievable is no discharge of process waste water pollutants for the manufacture of the following chemicals:

Phosphorus Consuming Subcategory
- Phosphorus (and Ferrophosphorus)

Phosphorus Consuming Subcategory
- Phosphoric Acid (Dry Process)
- Phosphorus Pentoxide
- Phosphorus Pentasulfide
- Phosphorus Trichloride
- Phosphorus Oxychloride

Phosphate Subcategory
- Sodium Tripolyphosphate
- Calcium Phosphates (Food Grade)
- Calcium Phosphates (Animal Feed Grade)

The recommended new source performance standards are the same as the above recommended best available technology economically achievable.

SECTION III

INTRODUCTION

PURPOSE AND AUTHORITY

Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) to the Act. Section 306 of the Act requires the achievement by new sources of a standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operation methods and other alternatives. The regulations proposed herein set forth effluent limitation guidelines pursuant to Section 304(b) of the Act for the phosphate manufacturing point source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b)(1)(A) of the Act, to propose regulations establishing Federal standards of performances for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcements of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the phosphate manufacturing source category, which was included within the list published January 16, 1973.

SUMMARY OF DEVELOPMENT METHODS

The Environmental Protection Agency has determined that a rigorous approach including plant surveying and verification testing is necessary for the promulgation of effluent standards from industrial sources. A systematic approach to the achievement of the required guidelines and standards includes the following:

(a) Categorization of the industry and determination of those industrial categories for which separate effluent limitations and standards need to be set;

(b) Characterization of the waste loads resulting from discharge within industrial categories and subcategories;

(c) Identification of the range of control and treatment technology within each industrial category and subcategory;

(d) Identification of those plants having the best practical technology currently available (notable plants); and

(e) Generation of supporting verification data for the best practical technology including actual sampling of plant effluents by field teams.

The culmination of these activities is the development of the guidelines and standards based on the best practicable current technology. This report describes the results obtained from application of the above approach to the phosphate manufacturing industry, as defined for the purpose of this study as the following list of products:

Elemental Phosphorus and Ferrophosphorus
Dry-Process Phosphoric Acid
Phosphorus Pentoxide
Phosphorus Pentasulfide
Phosphorus Trichloride
Phosphorus Oxychloride
Sodium Tripolyphosphate
Calcium Phosphates (Non-Fertilizer)

The effluent limitation guidelines and standards of performance proposed herein were developed in the following manner. The point source category was first subcategorized for the purpose of determining whether separate limitations and standards are appropriate for different segments within a point source category. Such subcategorization was based upon raw material used, product produced, manufacturing process employed, and other factors. The raw waste characteristics for each subcategory were then identified. This included an analysis of (1) the source and volume of water used in the process employed and the sources of waste and waste waters in the plant; and (2) the constituents (including thermal) of all waste waters including toxic constituents which result in taste, odor, and color in water or aquatic organisms. The constituents of waste waters which should be subject to effluent limitation guidelines and standards of performance were identified.

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The full range of control and treatment technologies existing within each subcategory was identified. This included an identification of each distinct control and treatment technology, including both in-plant and end-of-process technologies, which are existent or capable of being designed for each subcategory. It also included an identification in terms of the amount of constituents (including thermal). The chemical, physical, and biological characteristics of pollutants of the effluent level resulting from the application of each of the treatment and control technology and the required implementation time were also identified. In addition, the non-water quality environmental impact, such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, noise and radiation, were also identified. The energy requirement of each of the control and treatment technologies was identified as well as the cost of the application of such technologies.

The information, as outlined above, was then evaluated to determine what levels of technology constituted the best practicable control technology currently available, "best available technology economically achievable" and the "best available demonstrated control technology, processes, operating methods, or other alternatives". In identifying such technologies, various factors were considered. These included the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the process employed, the engineering aspects, process changes, non-water quality environmental impact (including energy requirements), and other factors.

The data for identification and analyses were derived from a number of sources. These sources included EPA research information, published literature, previous EPA technical guidance for inorganic chemicals, alkali and chlorine industries, qualified technical consultation, and on-site visits and interviews at notable manufacturing plants throughout the United States. All references used in developing the guidelines for effluent limitations and standards of performance for new sources reported herein are included in Section XIII of this document. Five companies in the phosphate manufacturing industry were contacted. A breakdown of the data base is listed below:

Chemical	Number of Plants in Data Base			
	Literature	Inspected	Sampled	Permit Application
P_4	1	3	2*	2
H_3PO_4		2	1*	2
P_2O_5		1	1	1
P_2S_5		2	2	2
PCl_3		2	2	2
$POCl_3$		2	2	2
$Na_5P_3O_{10}$		2	1*	1
Calcium Phosphates				
(Food Grade)		1	1	1
(Feed Grade)		1	1	1

*Includes verification of plants with no discharge.

In addition much information was obtained from plant personnel at the time of plant inspections, plant sampling, and company discussions.

GENERAL DESCRIPTION OF THE INDUSTRY

The industry covered by this document is the phosphate manufacturing source category. It is more descriptively termed the nonfertilizer phosphorus industry. The following chemicals covered by SIC 2819 were studied:

- phosphorus
- ferrophosphorus
- phosphoric acid (dry process)
- phosphorus pentoxide
- phosphorus pentasulfide
- phoshporus trichloride
- phosphorus oxychloride
- sodium tripolyphosphate
- calcium phosphates (food grade)
- calcium phosphates (animal feed grade)

Other phosphorus and phosphate chemicals are expected to be covered at a later time.

The flow of materials in the phosphate manufacturing industry is depicted in Figure 1. This industry is almost entirely based upon the production of elemental phosphorus from mined phosphate rock. The economics have dictated that the phosphorus production facilities be located at the sources of the raw material, which are in three areas in the United States: Tennessee, the Idaho-Montana area, and Florida. The key in-plant siting decision is the relative weights of phosphate rock, elemental phosphorus and phosphoric acid (about 10:1:4). Hence, the rock is processed close to the mine and the acid is produced close to

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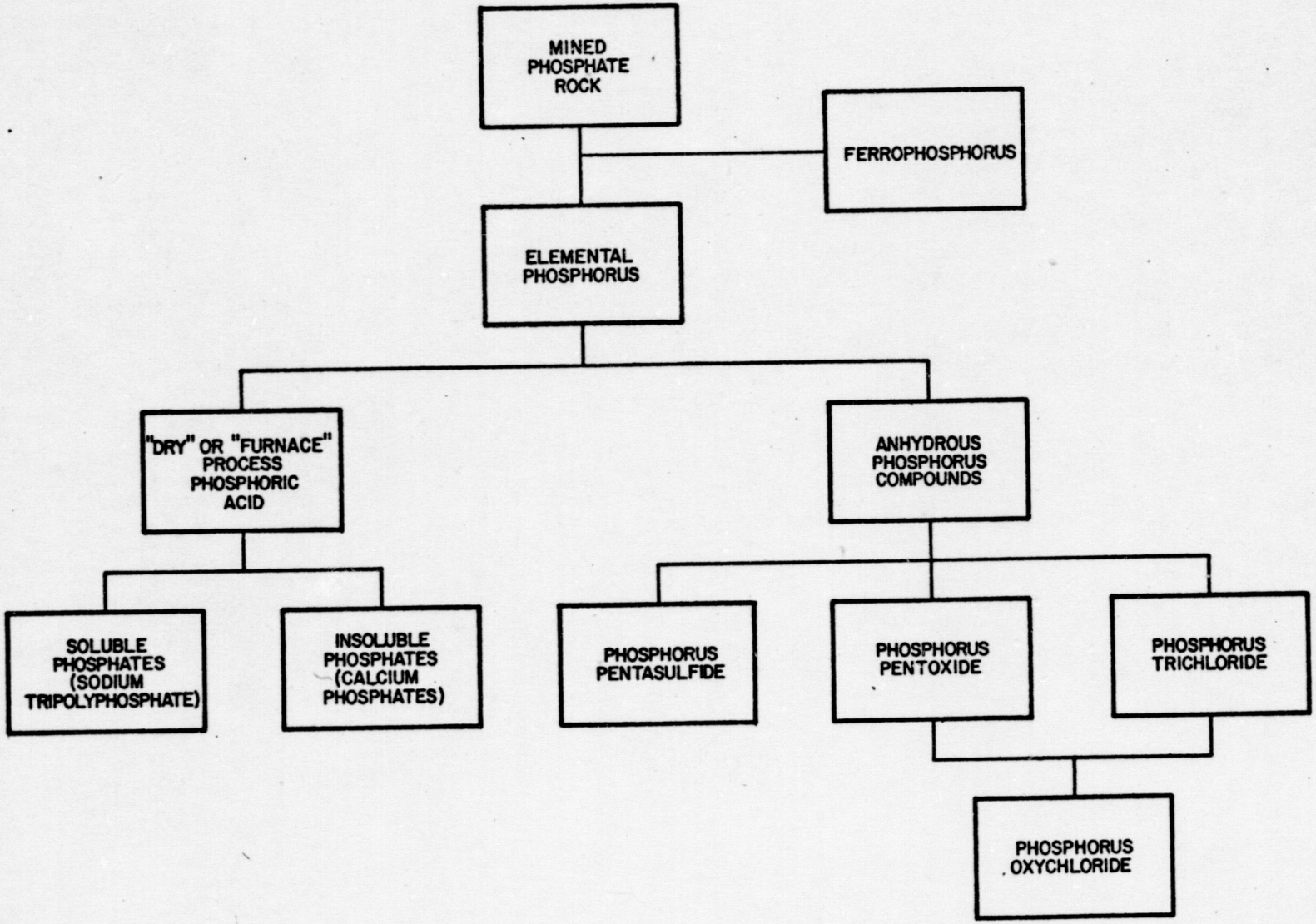


FIGURE 1

FLOW OF MATERIALS IN THE NON-FERTILIZER PHOSPHORUS CHEMICALS INDUSTRY

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its consumption point; the relatively low-weight elemental phosphorus is almost universally the form shipped from place to place.

Ferrophosphorus, widely used in the metallurgical industries, is a direct by-product of the phosphorus production process, since most furnace-grade phosphate rock contains 2 to 6 percent iron oxide.

Over 87 percent of the elemental phosphorus is used to manufacture high-grade phosphoric acid by the furnace or "dry" process (as opposed to the wet process which coverts phosphate rock directly into phosphoric acid; this lower-grade wet process acid is almost exclusively used in the fertilizer industry and is separately discussed in another portion of this EPA effort). The remainder of the elemental phosphorus is either marketed directly or converted to chemicals such as phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride. These later chemicals are chiefly used in synthesis in the organic chemicals industry.

Much of the furnace-grade phosphoric acid is directly marketed, largely to the food industry and to the high-grade fertilizer industry. Phosphoric acid is also used to manufacture two basic classes of phosphates: water-soluble phosphates used in detergents and for water treatment, typified by sodium tripolyphosphate; and water-insoluble phosphates which are used in animal feeds and in foods, typified by the calcium phosphates.

The process involved in the non-fertilizer phosphorus chemicals industry are very briefly as follows:

Elemental phosphorus and ferrophosphorus are manufactured by the reduction of phosphate rock by coke in very large electric furnaces, using silica as a flux. Very large quantities of water are circulated for cooling the very hot equipment, for cooling and granulating the slag, and for condensing the phosphorus vapor from the furnace. Since water is both non-reactive and immiscible with liquid phosphorus, water is used extensively in direct contact with phosphorus for heat transfer, for materials transfer, for protection from the atmosphere, and for purification. This study is concerned with manufacturing operations subsequent to receiving washed phosphate ores at the phosphorus production facility. Ore benefication is commonly but not exclusively conducted at a separate off-site location. The huge waste load from benefication, 7500 kg of gangue per kkg of phosphorus eventually produced, warrants a separate study as a segment of the mining industry.

Phosphoric acid manufactured by the "dry" or furnace process consists of the burning of liquid phosphorus in air, the subsequent quenching and hydrolysis of the P_2O_5 vapor, and the collection of the phosphoric acid mists. The operation uses cooling water and process water is consumed

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in making the aqueous acid. Solid wastes may be generated should a plant perform subsequent purification of the acid.

The manufacture of the anhydrous phosphorus chemicals (P_2O_5, P_2S_5, and PCl_3) is essentially by the direct union of phosphorus with the corresponding element. Phosphorus oxychloride, $POCl_3$, is manufactured from PCl_3 and air or from PCl_3, P_2O_5, and chlorine. Water use is limited to cooling water, to water for transferring elemental phosphorus, to scrubber water, and to wash water for reaction vessels and shipping containers.

Sodium tripolyphosphate is manufactured by the neutralization of phosphoric acid with the appropriate proportions of caustic soda and soda ash in mix tanks. The resulting mixture of monoand di-sodium phosphates is dried and the crystals calcined to produce the tripolyphosphate.

The calcium phosphates are similarly made by the neutralization of phosphoric acid with lime. The amount and type of lime used and the amount of water in the process determines whether anhydrous monocalcium phosphate, monocalcium phosphate monohydrate, dicalcium phosphate dihydrate, or tricalcium phosphate, is the final product. Table 2 lists production tonnages for these chemicals as reported by the U.S. Bureau of Census. As seen from this table the industry is relatively small relative to numbers of plants.

Table 3 lists the current selling prices of the chemicals within this industry. Table 4 lists the producers of phosphate products.

TABLE 2. U.S. Production Phosphates

Chemicals	Metric Tons	Short Tons	Number of Plants
Phosphorus	495,000	545,000	10
Ferrophosphorus	110,000*	121,000*	
Phosphoric Acid	1,640,000**	1,810,000**	25
(Furnace Process)			
Phosphorus Pentoxide	(withheld)	(withheld)	(withheld)
Phosphorus Pentasulfide	54,000	59,000	5
Phosphorus Trichloride	50,000	55,000	4
Phosphorus Oxychloride	28,000	31,000	4
Sodium Tripolyphosphate	945,000	1,040,000	17
Calcium Phosphates	536,000	592,000	7

*Independently estimated.(2)
**Estimated as 87 percent of Phosphorus Consumption, using 90 percent conversion, and stated as acid of 54 percent P_2O_5. The total production of phosphoric acid, both wet and dry was 5,650,000 kkg (6,240,000 short tons).

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TABLE 3. Current Selling Prices of Phosphorus Chemicals
Source: Chemical Marketing Reporter, June 25, 1973

CHEMICAL	GRADE	SELLING PRICE	
		$/Metric Ton	$/Short Ton
White Phosphorus		419	380
Phosphoric Acid (Furnace)	75% Commercial & Feed	164	149
	80% Commercial & Feed	176	160
	85% National Formulary	194	176
Phosphorus Pentoxide		441	400
Phosphorus Pentasulfide		299	271
Phosphorus Trichloride		292	265
Phosphorus Oxychloride		270	245
Sodium Tripolyphosphate	Technical	179	162
	Food	270	245
Monocalcium Phosphate	Anhydrous Food	314	285
Dicalcium Phosphate	U.S.P Food	286	259
	Feed	82	74
Tricalcium Phosphate	NF Precip.	315	286

TABLE 4

Producers of Phosphate Products

	Phosphorous	Phosphorous Pentoxide	Phosphorous Trichloride	Phosphorous Oxychloride	Phosphorous Pentasulfide	Furnace Acid	Sodium Tripolyphosphate	Feedstock Dicalcium Phosphate	Technical Calcium Phosphate
Holmes Company	0					0	0		
FMC Corporation	0		0	0		0	0		
Mobil Corporation	0		0			0	0		0
Monsanto Company	0		0	0	0	0	0	0	
Occidental Petroleum Corp.	0	0	0	0	0	0	0		0
Stauffer Chemical	0	0	0	0	0	0			
TVA	0					0	0		
Olin Corporation						0		0	
Goodpasture, Inc.								0	
American Cyanamid Co.								0	0
Borden, Inc.									0
Eastman Kodak Co.								0	
Farmland Industries								0	
Int'l. Minerals & Chemical Corp.									0
Knox Gelatine, Inc									0
Richardson-Merrell, Inc.									

DETAILED PROCESS DESCRIPTIONS

Following is a description of each process in this industry. Process flow disgrams are included. In generating the following process descriptions, emphasis has been placed upon process features which generate aqueous wastes. The details of the waste stream character, however, have been left for discussion in Section V.

Much of the process data in this section was acquired by discussions with industry personnel and by observations of existing facilities. A large body of data also exists in the published literature, and was used extensively in the following discussion. Of particular usefulness were the publications of Beveridge and Hill,(4) of Barber,(5,6) Barber and Farr,(7) and LeMay and Metcalf(8) of The Tennessee Valley Authority, which supplied very specific operating details of TVA's facilities; of Ellwood,(9) and of Bryant, Holloway and Silber(10) of the Mobil Chemical Company. Standard reference books such as Faith, Keyes and Clark,(11) Kirk and Othmer,(12) and Shreve,(13) were also useful.

THE PHOSPHORUS PRODUCTION SEGMENT

Phosphorus is manufactured by the reduction of mined phosphate rock by coke in an electric furnace, with silica used as a flux. Slag, ferrophosphorus (from iron in the phosphate rock) and carbon monoxide are reaction by-products. The simplified overall reaction may be written:

$$2Ca_3(PO_4)_2 + 10\,C + 6SiO_2 \xrightarrow{1250 - 1500^{\circ}C} P_4 + 10\,CO + 6CaSiO_3.$$

A typical material balance for the process is:

Raw Materials		Products	
Phosphate Rock	10.0 kkg	Phosphorus	1.0 kkg
Silica	1.5	Ferrophosphorus	0.3
Coke	1.5	Slag	8.9
		Carbon Monoxide	2.8
Total	13.0 kkg	Total	13.0 kkg

The electrical power consumption is approximately 15,400 KWH/kkg (14,000 KWH/ton) of phosphorus produced; part of this supplies the endothermic heat of reaction of 6,200 KWH/kkg of P_4.

The standard process, as pictured in Figure 2, consists of three basic parts: phosphate rock preparation, smelting in the electric furnace, and recovery of phosphorus.

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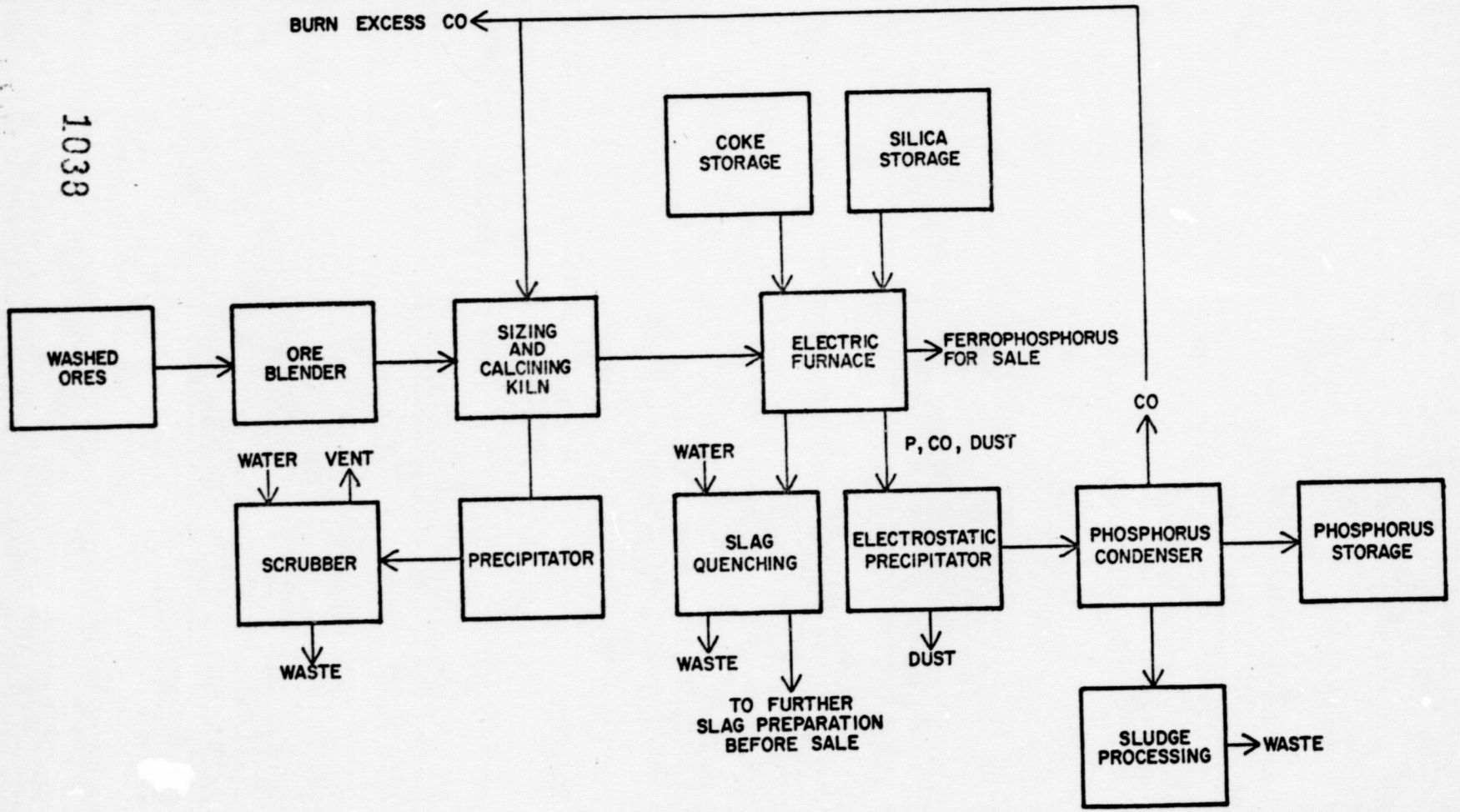


FIGURE 2
STANDARD PHOSPHORUS PROCESS FLOW DIAGRAM

Phosphate rock ores are first blended so that the furnace feed is of uniform composition. The silica composition is important since the overall furnace feed must have a SiO_2/CaO ratio close to the eutectic composition for desired slag flow properties. The blended phosphate rock is carefully pretreated by drying, by agglomerating the particles, and by heat treating.

After the raw phosphate rock is dried, sizing or agglomeration is accomplished by pelletizing, briquetting, flaking, or "nodulizing", and pre-formed agglomerates are then calcined in a rotary kiln. The nodulizing operation performs simultaneous agglomeration and calcining by heating the rock to its incipient fusion point, with subsequent crushing, sizing, and recycling of fines. Sizing promotes the even distribution of gas flow within the furnace and results in more efficient heat transfer and lower total energy costs. The size of the furnaces has dramatically increased in recent years, accentuating the needs for stoichiometric balance and thermal homogeneity within the charge (or "burden"). Heat treatment or calcining of the feed increases the strength and hardness of the particles, preventing large quantities of fines from being formed by attrition.

The calcining, at 1000 to 1400°C, also liberates water of hydration, organics, carbon dioxide, and fluorine at a much lower energy cost than would be required in the subsequent electric furnace operation. Since 25 percent of the manufacturing costs of phosphorus are for electric power, considerable effort is made to conserve this power. Moreover, by-product carbon monoxide from the smelting operation is available as a source of auxiliary energy.

The sizing and calcining operations are sources of dust and of fluorine fumes. The dust may be electrostatically precipitated, and the gases are scrubbed with water, removing fluorine as HF and H_2SiF_6. The dry dusts collected are normally recycled to the nodulizing operation.
The burden of treated phosphate rock, coke, and sand is charged to the furnace by incrementally adding weighed quantities of each of the three materials to a common belt conveyor. The furnace itself has a carbon crucible and carbon-lined steel sidewalls, with a two-foot-thick self-supporting cast concrete roof. In an effort to eliminate periodic roof replacement due to excessive cracking of the concrete, some newer furnaces have anti-magnetic (to avoid induction heating) stainless steel roof structures. Penetrations in the furnace are for feed chutes, for carbon electrodes, for tap holes, for slag (upper liquid layer) and for ferrophosphorus (lower liquid layer), and for exhaust gases.

Electric furnaces for phosphorus production have been dramatically increasing in size to achieve operating economies:

Year	Size of Largest Furnace in Operation		
	Megawatts	kkg/Year	Tons/Year
1950	25	13,600	15,000
1960	50	27,200	30,000
1970	65	36,300	40,000

The smallest furnaces produce 9,100 kkg (10,000 tons) of phosphorus per year.

An appreciation of the physical size may be attained from the fact that the largest carbon electrodes used are 1.5 to 1.8 meters (5 to 6 feet) in diameter and carry 50,000 amps each.

The furnace is extensively water-cooled. Cooling water is used for the electrical transformer, for the furnace shell, for the crucible bottom, for the fume hood, for the tapholes, and for electrode joints. Newer furnaces use telescoping water seals on furnace electrodes; and for TVA-type furnaces with rotating crucibles, a water seal is provided between the crucible and the stationary roof.

The 2 to 6 percent Fe_2O_3 in the furnace-grade phosphate rock is reduced, with the iron recovered as the ferrophosphorus alloy:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$
$$8Fe + P_4 \rightarrow 4Fe_2P$$

The ferrophosphorus typically contains 59 percent iron and 22 percent phosphorus and is marketed for the production of phosphorus alloys. The vanadium content of ferrophosphorus adds to its value. Should the marketplace be favorable for ferrophosphorus, iron slugs can be added to the furnace charge. Alternately, should a soft market for ferrophosphorus occur, the ferrophosphorus can be converted into high-grade metallurgical iron and fertilizer phosphates. An important degree of freedom is in the ore blending operation, where ores of appropriate iron content may be selected depending upon the ferrophosphorus market.

Slag and ferrophosphorus are tapped periodically. The air cooled ferrophosphorus is sold in lumps to the metallurgical industry; no water is involved either in ferrophosphorus cooling or in subsequent product preparation.

The slag may typically contain 38 percent SiO_2 and 48 percent CaO, and also contain considerable quantities (depending of course upon the ore composition) of Al_2O_3, CaF_2, K_2O, and MgO, with traces of uranium and other heavy metals. The slag may be air-cooled, but water quenching is more typical. High-density slag is produced by adding water to molten slag in a pit, and by subsequently breaking it up and shipping aggregate for railroad bed or roadbed construction. Alternately, a high-velocity

water stream may be used upon the molten slag to produce a low density expanded or granulated slag, which has a market in concrete formulation. In either event, some of the fluorides from the slag are captured by the quenching water, either as soluble fluorides or as suspended solids.

There are numerous sources of fumes from the furnace operation. The feeding operation is a source of dust, and fumes are emitted from the electrode penetrations and from the tapping operations. These fumes, consisting of dust, phosphorus vapor (which is immediately oxidized to phosphorus pentoxide), and carbon monoxide are often collected and scrubbed.

The hot furnace gases, consisting of 90 percent CO and 10 percent P_4, pass through an electrostatic precipitator to remove the dust prior to phosphorus condensation. Unless this dust were removed, it would later be emulsified by liquid phosphorus and water, forming large amounts of "phosphorus mud" or sludge which would be difficult and costly to handle.

The precipitator is a most unusual piece of equipment. In the phosphorus process, the precipitator is in the main process stream, as opposed to its usual application in an exhaust stream. Because of this, it is gas-tight (especially since any air would cause phosphorus combustion). It operates at very high temperatures with the inlet gas approaching 540°C (1000°F), and its surfaces must be maintained hot to prevent phosphorus condensation (the dew point of phosphorus is 180°C (356°F)). The precipitator is typically a tube bundle, with the gas passing through the tubes, and with a high-voltage wire along the axis of each tube. Both the wire and the tube are mechanically shaken to release the dust into a hopper. In some installations, the dust is slurried in water, pumped to a settling pond, and the solids are recycled to the raw feed for recovery of phosphates values (the clarified pond effluent is reused in the slurrying operation).

The high-voltage wires may be insulated from the shell with an oil seal; contaminated oil is periodically replaced with fresh oil. Alternately, a quartz seal may be used. The entire unit is heated either electrically or by an inert gas jacket of by- product carbon monoxide combustion gases.

Downstream of the precipitator, the phosphorus is condensed by direct impingement of a hot water spray, which is sometimes augmented by heat-transfer through water-cooled condenser walls. The liquid phosphorus (freezing point 44°C (111°F)) drains into a water sump, where the water maintains a seal from the atmosphere. This water is partially neutralized by addition of ammonia or caustic to minimize corrosion, and then is recirculated from the sump to the phosphorus condenser.

Liquid phosphorus is stored in steam-heated tanks under a water blanket and is transferred into tank cars by pumping or by hot water displacement. The tank cars also have a protective blanket of water and are equipped with steam coils for remelting at the destination.

Despite very high precipitator removal efficiencies, enough dust reaches the condensers to form some phosphorus mud, which is typically 10 percent dust, 30 percent water, and 60 percent phosphorus.

The condenser exhaust gases are mainly carbon monoxide, which is either burned in a flare or utilized for heating elsewhere in the plant.

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THE PHOSPHORUS-CONSUMING SEGMENT

Phosphoric Acid (Dry Process)

Phosphoric acid is made from elemental phosphorus in the "dry" process, as opposed to the acidulation of phosphate rock in the "wet" process. The wet process is discussed in a separate report, dealing with the fertilizer industry, in this overall EPA effort. Furnace acid, as dry-process phosphoric acid is called, is relatively pure compared to wet-process acid, as Table 5 indicates. Consequently, the furnace acid is primarily used for preparing foodstuffs, detergents, and other high-grade products; while wet acid is primarily used for preparing fertilizers and animal feed supplements.

TABLE 5. Impurities in Phosphoric Acid (54% P_2O_5)

	Wet Process Acid	Furnace Acid
F, wt %	0.6 - 1.0	0.007
SO_3, wt %	2.7	0.003
Al_2O_3, wt %	0.9	0.001
Fe_2O_3, wt %	1.2	0.0007
Water insolubles, wt %	0.8	
Total Impurities, wt %	6.2 - 6.6	0.012
Density, kg/l (lb/gal) @ 27°C (80°F)	1.72 (14.3)	1.57 (13.1)
Viscosity, cp @ 27°C (80°F)	85	18
Color	Black	Colorless

In the standard dry process illustrated in Figure 3, liquid phosphorus is burned in air, the resulting gaseous phosphorus pentoxide is absorbed and hydrated in a spray of water, and the mist is collected with an electrostatic precipitator.

The standard reaction may be written:

$$P_4 + 5O_2 \rightarrow 2P_2O_5 + 6H_2O \rightarrow 4H_3PO_4$$

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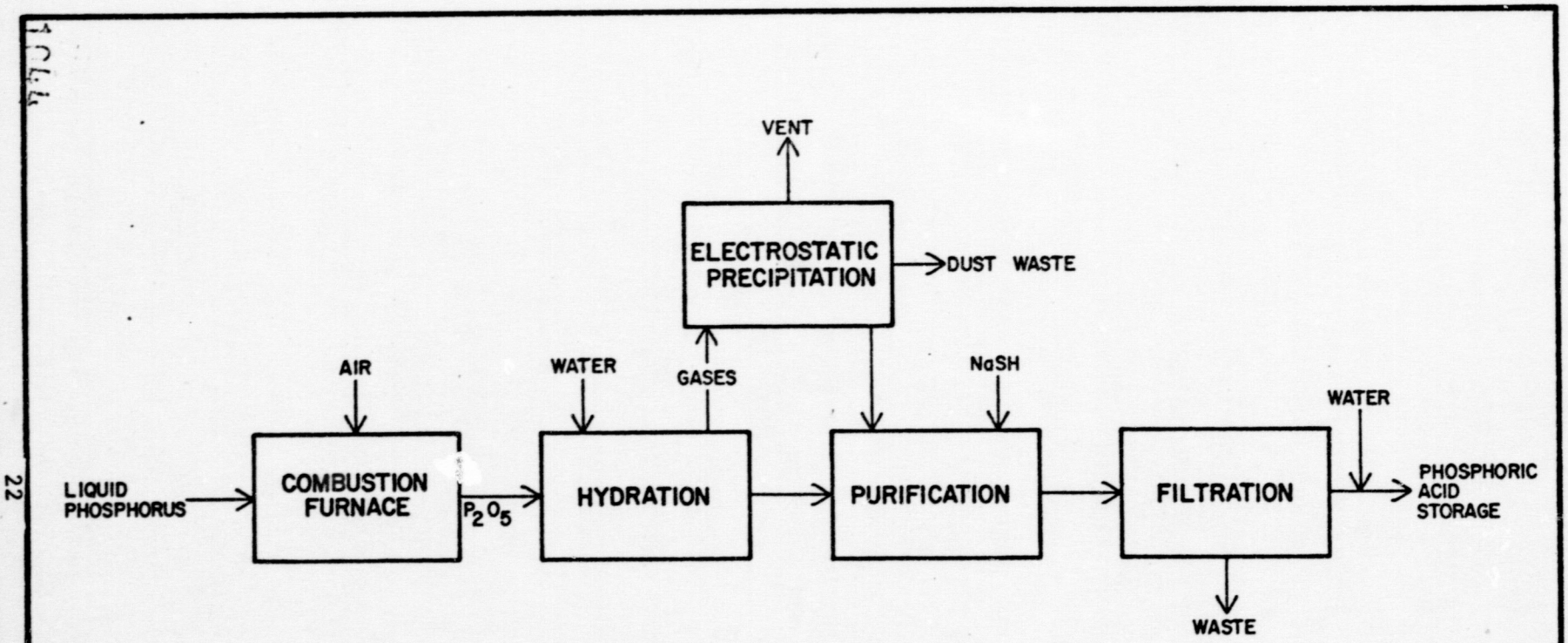


FIGURE 3
STANDARD PHOSPHORIC ACID FLOW DIAGRAM (DRY PROCESS)

Liquid phosphorus is stored under water in tanks heated with steam coils (the freezing point of phosphorus is 44°C (111°F)). The phosphorus may be fed to the burner by hot-water displacement in a feed tank, in a loop with a steam-heated displacement water tank and water pump. Alternately, the liquid phosphorus may be pumped directly.

There are variations in the design of the liquid phosphorus injector. Some producers achieve fine atomization using air in a dual-fluid injector (where the injection orifice can be large enough to prevent plugging). To prevent freezing of the phosphorus in upstream portions of the injector and yet to keep the injector tip cool, intricate use of both steam and cooling water has been simultaneously applied. Other designs have proven successful for phosphorus atomization, including the exploitation of extreme turbulence in a pre-combustion zone. Some form of temperature control is required, since red phosphorus formed at combustion temperatures much higher than 1650°C (3000°F) would color the resulting acid and would plug injector orifices.

In the combustion chamber, corrosion by P_2O_5 vapors and by hot phosphoric acid (formed from the moisture in the air) is countered by using a graphite lining. The steel shell of the combustion chamber is cooled by running water down its exterior surfaces. This mode of heat transfer is standard, pressurized cooling water is avoided since any leaks would result in premature hydration. Recent plants have been constructed with stainless steel combustion chambers.

The gas exiting from the combustion chamber is typically 540°C (1000°F), and is then hydrated with direct water sprays, which also reduces the temperature to 120°C (250°F) or less.

A variation of the standard process, illustrated in Figure 4, uses dilute acid for hydration instead of water. In this case, the make-up water is added in the vapor-liquid separation step. The rationale is that P_2O_5 vapor is absorbed more easily as the concentration of absorbing acid is increased. Another deviation from the standard process, also shown in Figure 4, is the use of a high-pressure-drop venturi scrubber to complete the somewhat difficult hydration, and a screen-type demister and separation tower instead of an electrostatic precipitator to fr[illegible] the tail gases of the persistent acid mist.

When an electrostatic precipitator is used for collection of the phosphoric acid mist, the corrosivity requires the use of carbon tubes and stainless steel high-voltage wires. Those plants using a high-pressure-drop venturi scrubber and a screen type demister with a separation tower utilize stainless steel construction. Where dilute phosphoric acid is used in the hydrator, the make-up water is added in the separation tower. Regardless of process variation, phosphoric acid

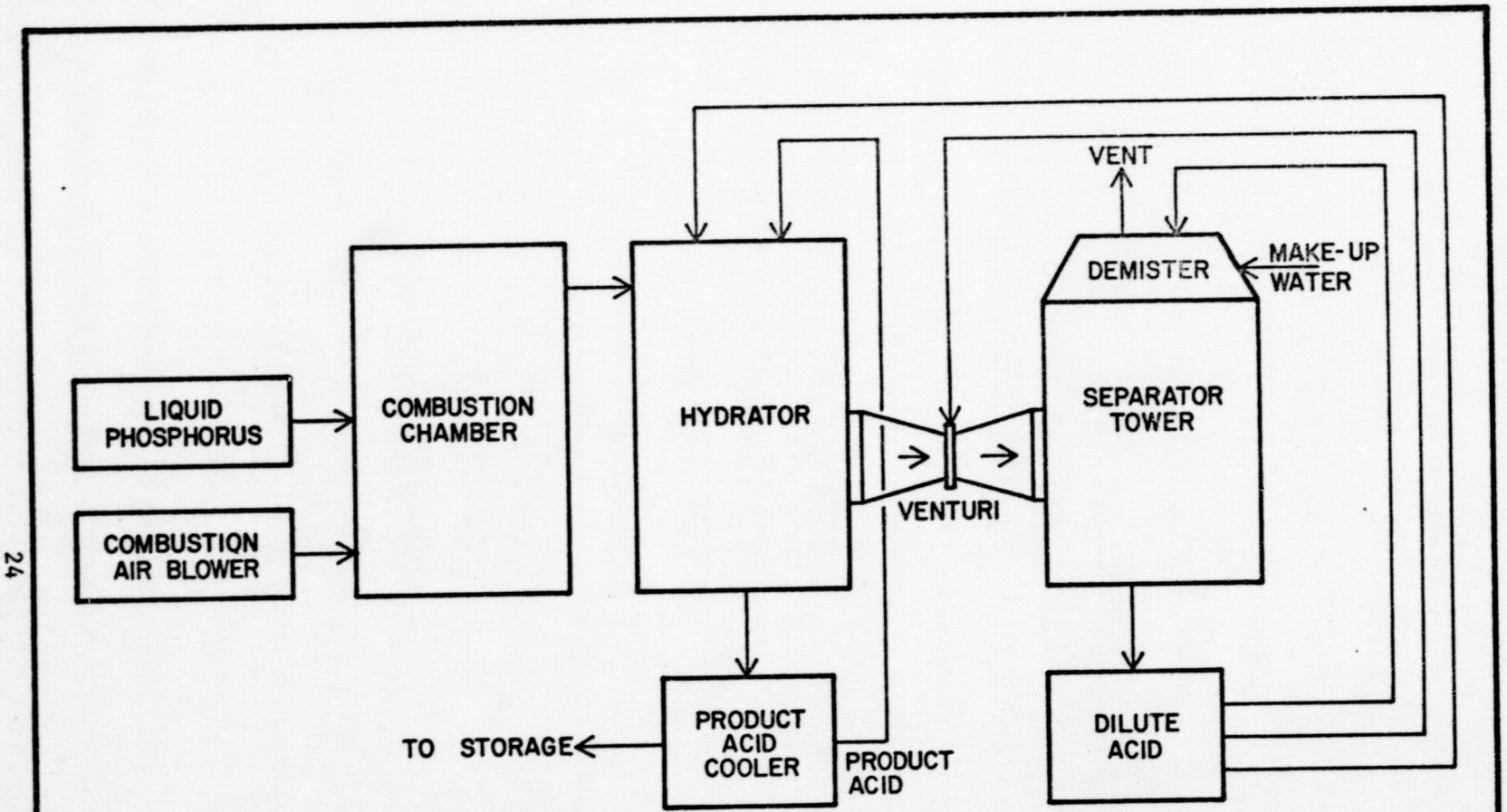


FIGURE 4
VARIATIONS OF PHOSPHORIC ACID (DRY) PROCESS

is made with a consumption of water; no aqueous waste streams are generated by the process.

The product acid is quite pure, but for the manufacture of foodgrade acid, traces of arsenic must be removed. Arsenic occurs naturally with phosphorus in the ore (they are both Group V-A elements) at a level of about 0.075 kg of arsenic per kkg of phosphorus (0.15 lb/ton). The arsenic is quantitatively carried through into the acid, and is commonly removed by treatment with a soluble sulfide followed by filtration of the insoluble arsenic sulfide.

Phosphorus Pentoxide

The manufacture of solid anhydrous phosphorus pentoxide is similar to the first stages of phosphoric acid manufacture. Liquid phosphorus is burned in an excess of air:

$$P_4(l) + 5O_2 \rightarrow 2P_2O_5(s)$$

Figure 5 is a flow diagram for a standard phosphorus pentoxide manufacturing facility. A significant difference between the two processes is that in the anhydrous phosphorus pentoxide process, the air is dried to an extremely low dew point, since any moisture results in a lumpy and agglomerated product not suited for its uses as a reactive drying agent and as a reactive condensing agent in organic synthesis. Typically, the ambient air is filtered, then refrigerated to achieve a dew point of -18 to -7°C (0 to 20°F), and then dried to a dew point of -46°C (-50°F) with silica gel.

After reaction of liquid phosphorus with excess dried air in the combustion chamber, the P_2O_5 vapor is condensed to a solid in a "barn", which is a room-like structure. Some installations utilize a more conventional tower for condensation. Both the combustion chamber and the barn (or tower) are cooled by an external flow of water down the surfaces; pressurized cooling water is avoided since any leaks would result in lumpy, unacceptable product.

Condensed phosphorus pentoxide solid is mechanically scraped from the walls using moving chains, and is discharged from the bottom of the barn or tower with a screw-type conveyor. The gases are vented to the atmosphere through a tail-gas water seal which absorbs any P_2O_5 vapor or solid carry-over. There is usually continuous water addition and overflow for the tail gas seal.

The product particle size is sensitive to the rate of cooling and condensation in the barn or tower. In a barn, the external surface-to-volume ratio is small, a relatively high temperature is maintained in the condensing unit, and rather large crystals may grow. In a tower, heat transfer is more rapid, and the product is very finely divided.

One installation uses two towers in series; the first has much higher heat transfer rates and results in a coarser product than the second, and the products from the two towers are separately packaged.

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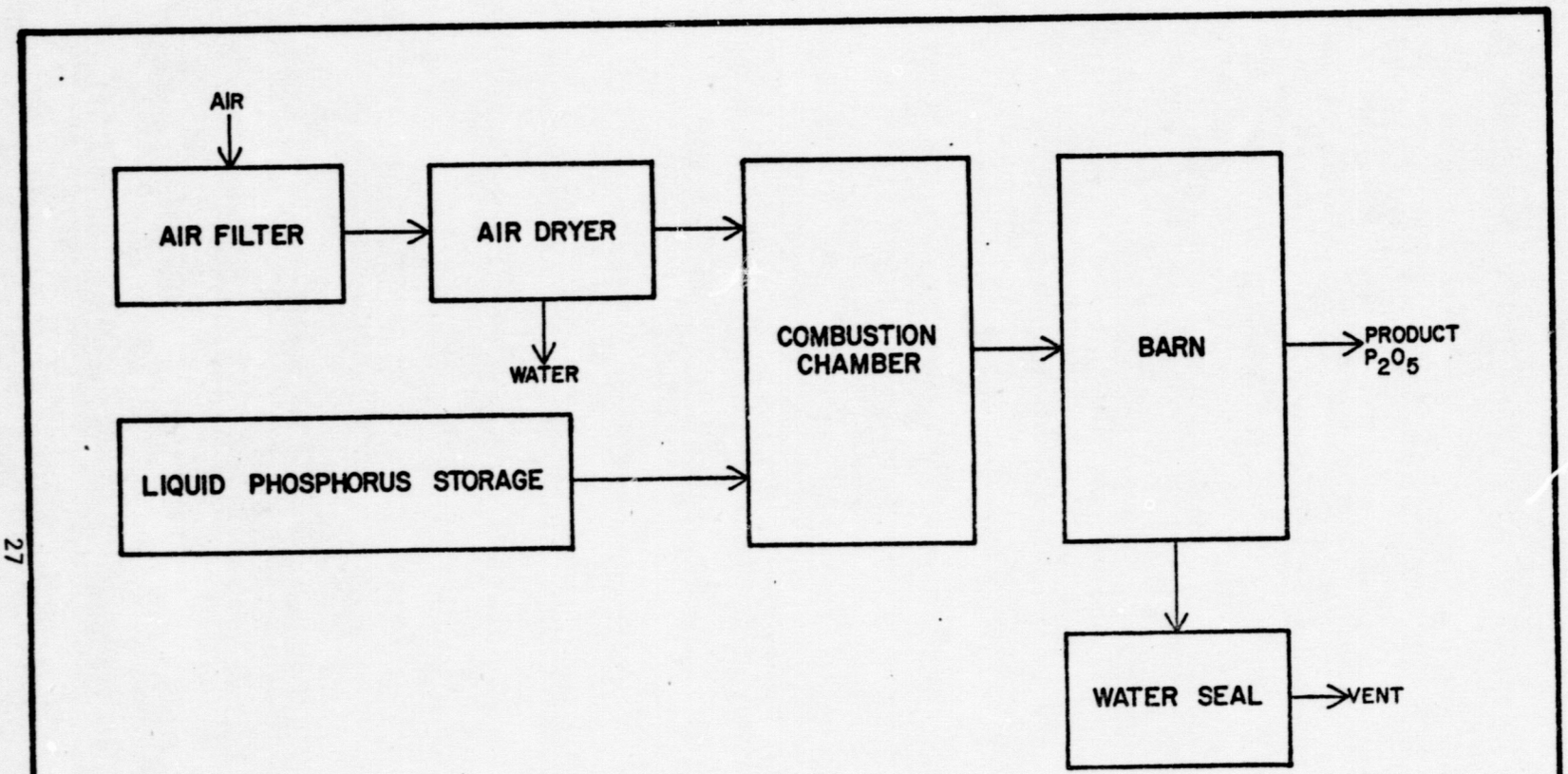


FIGURE 5
PHOSPHORUS PENTOXIDE MANUFACTURE FLOW DIAGRAM

1049

Phosphorus Pentasulfide

The standard process for the manufacture of phosphorus pentasulfide, shown in Figure 6, is by direct union of the elements, both in liquid form:

$$P_4(l) + 10S(l) \rightarrow 2P_2S_5(l)$$

The largest use of phosphorus pentasulfide is for the manufacture of lubricating oil additives.

Liquid sulfur (melting point 113°C (230°F)) is transferred from a steam-heated storage tank using submerged pumps, and liquid phosphorus (melting point 44°C (111°F)) is transferred by hotwater displacement. The highly exothermic reaction is usually carried out as a batch operation in stirred cast-iron pots. A "heel" of molten P_2S_5 (melting point 282°C (540°F)) from the previous batch is used to absorb the initial heat of reaction. Liquid phosphorus and liquid sulfur are incrementally added. Since the reactants and the product are extremely flammable at the reaction temperature, the reactor is continuously purged with nitrogen. A water seal is used in the vent line.

The batches from multiple reactors are forced into an electrically-heated (300°C (570°F)) P_2S_5 holding tank by nitrogen pressure. Some of the P_2S_5 is converted directly into product, while the rest is purified. Liquid P_2S_5 from the holding tank that is to be sold is cast directly into drums or into cones. When the molten product contacts air during casting, it ignites and fumes of P_2O_5 and SO_2 are generated. A fume hood and water scrubber are used. The cones, after cooling, are crushed and packaged; solid P_2S_5 does not auto-ignite in air. The dust from the crushing operation is removed in a dry separation system such as a cyclone.

The liquid P_2S_5 that is to be purified may be vacuum distilled (normal boiling point is 515°C (960°F)) in a continuous system. The condenser is cooled by a high-temperature heat transfer fluid, which in turn is cooled in a water-cooled heat exchanger. The condenser is operated between the melting and boiling points of the product. Molten purified P_2S_5 is then cast and crushed, sharing the fume scrubber and dust collection systems with the impure product operation.

An alternate mode of purification is the washing of crushed P_2S_5 with carbon disulfide, in which by-product phosphorus sesquisulfide (P_4S_3) and free sulfur are soluble.

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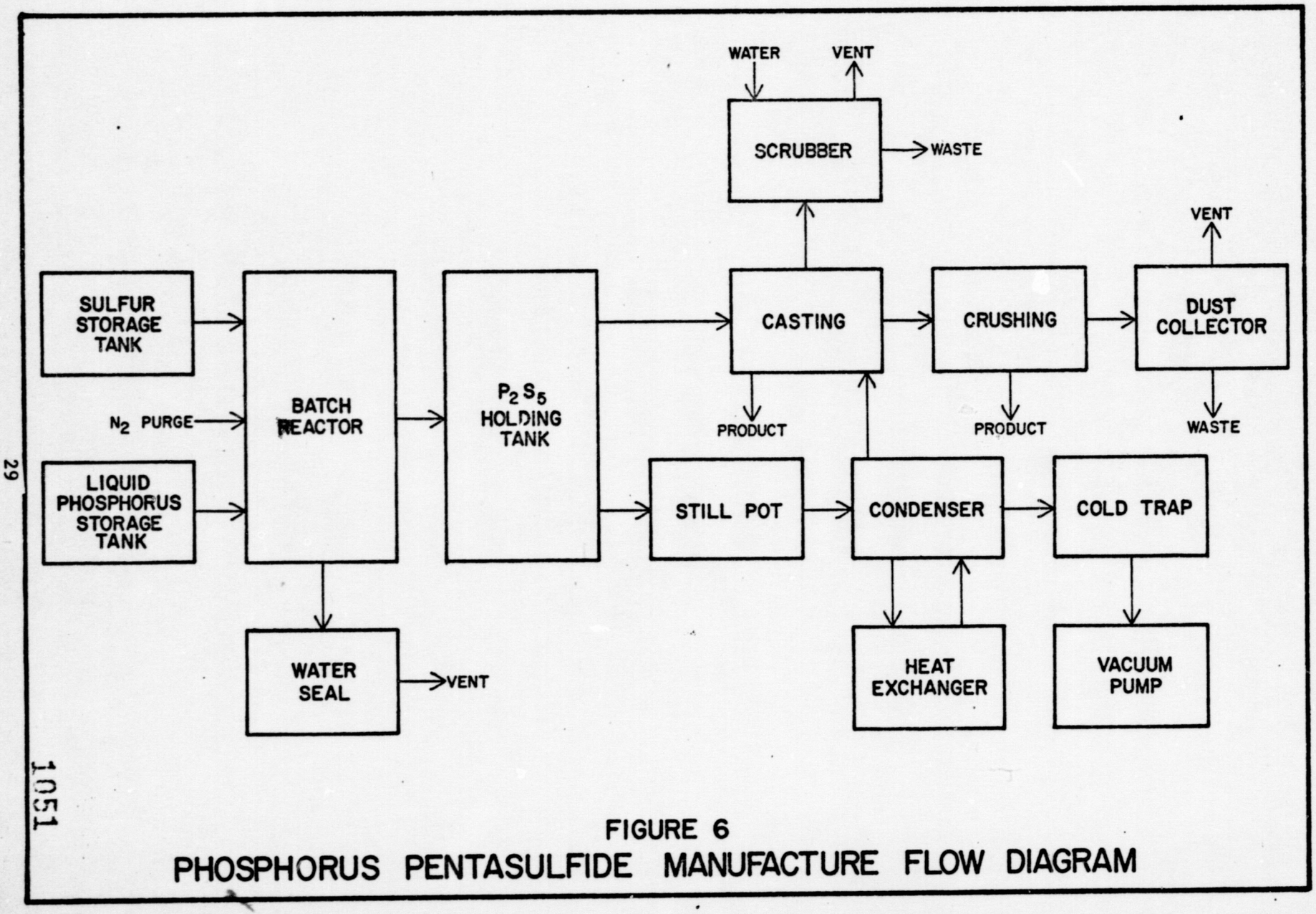


FIGURE 6

PHOSPHORUS PENTASULFIDE MANUFACTURE FLOW DIAGRAM

1051

Phosphorus Trichloride

Phosphorus trichloride, used extensively in organic synthesis, is manufactured directly from the elements:

$$P_4(l) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$

The standard process is shown in Figure 7. Liquid phosphorus is charged to a jacketed batch reactor. Chlorine is bubbled through the charge, and phosphorus trichloride product (melting point -112°C (-173°F)), boiling point 74°C (165°F) is refluxed until all of the phosphorus is consumed. Some cooling water is used in the reactor jacket since the formation of PCl_3 is exothermic. Care is taken to avoid an excess of chlorine; otherwise, phosphorus pentachloride is formed.

When the reaction is complete, the cooling water to the reflux condenser is turned off, steam is supplied to the reactor jacket, and the product of the batch distillation is condensed and collected.

A water scrubber collects hydrochloric acid and phosphorous acid, the hydrolysis products of PCl_3 vapors:

$$PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$$

The vapor pressure of the product is sufficiently high so that the fumes from transferring the product into shipping containers are also collected and scrubbed.

In a variation of the standard process, the reaction is conducted semi-continuously instead of batch-wise. The reflux condenser of Figure 7 is tailored so that only a small fraction of the PCl_3 is withdrawn as product; the larger fraction of condensed PCl_3 returns to the reactor and serves as the working fluid and heat sink for the reaction, since elemental phosphorus is somewhat soluble in PCl_3. Gaseous chlorine is added continuously, and liquid phosphorus is added incrementally.

No provision is generally made for continuous or frequent withdrawal of residue from the reactor either in the batch process or in the semi-continuous process. Instead, the residue is permitted to accumulate, and the reactor is shut down for cleanout at infrequent intervals.

Phosphorus trichloride is corrosive and is often shipped in returnable nickel drums. Prior to use, these drums are thoroughly washed with water and steam-cleaned. Some recent use has been made of non-returnable epoxy-lined steel drums.

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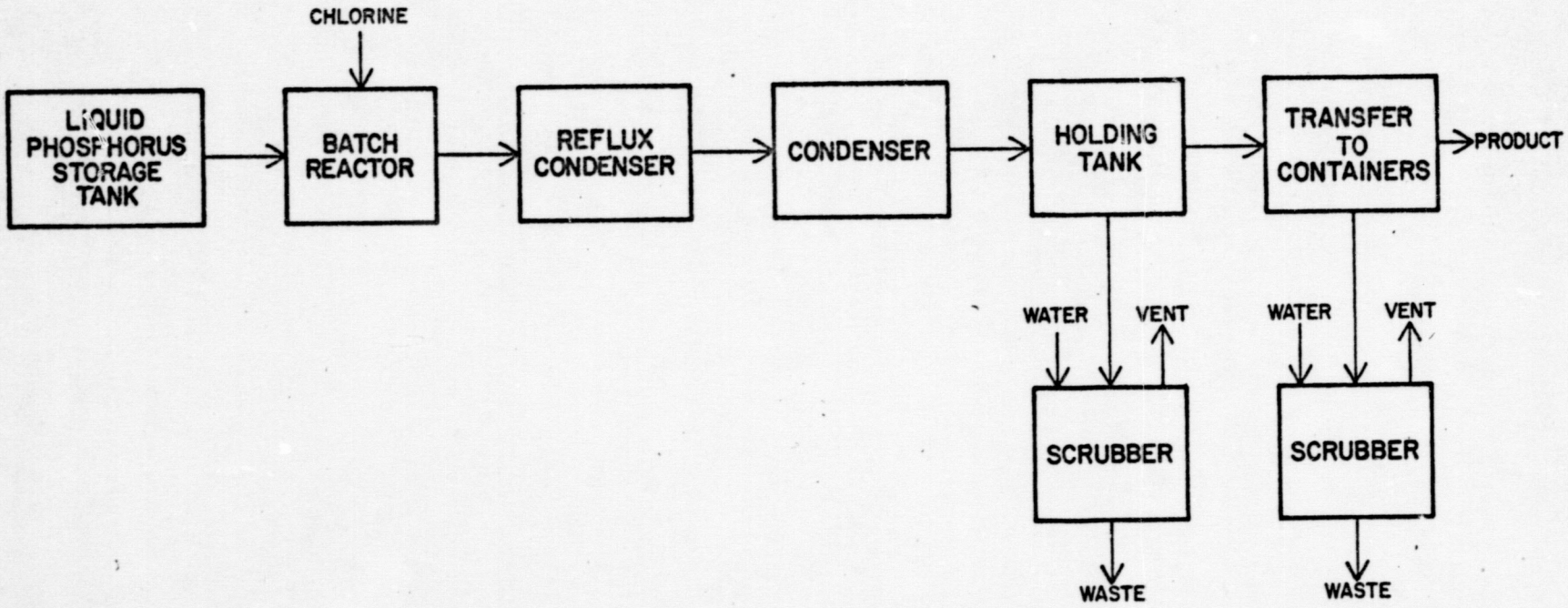


FIGURE 7

PHOSPHORUS TRICHLORIDE MANUFACTURE FLOW DIAGRAM

1053

Phosphorus Oxychloride

Phosphorus oxychloride, used in the preparation of organic phosphate esters and pharmaceuticals, is manufactured by the reaction of liquid phosphorus trichloride, chlorine, and solid phosphorus pentoxide:

$$3\ PCl_3(l) + 3\ Cl_2(g) + P_2O_5(s) \rightarrow 5\ POCl_3\ (l)$$

The standard process, illustrated in Figure 8, is carried out in a batch reactor and still very similar to the standard phosphorus trichloride equipment. Liquid phosphorus trichloride is charged to the reactor, solid phosphorus pentoxide is added, and chlorine is bubbled through the mixture while the PCl_3 (boiling point 74°C (165°F)) and later the $POCl_3$ (boiling point 105°C (221°F)) are refluxed. When the reaction is complete, steam is supplied to the reactor jacket, the water to the reflux condenser is shut off, and the product is distilled over and collected.

An alternate process for the manufacture of phosphorus oxychloride from phosphorus trichloride is also in commercial use. As is shown in Figure 9, dried air is used as the oxidant in a batch process. A water-cooled reflux condenser is used as in the standard process, except that a refrigerated condenser is added in series to ensure total reflux of the PCl_3 upstream of a water scrubber for the tail gas. The significant difference is that in the air-oxidation process, a large quantity of non-condensible gas (nitrogen and excess oxygen) is involved.

Instead of a final distillation step, the product $POCl_3$ is filtered, with periodic changing of the cartridge filter elements.

Water scrubbers collect hydrochloric acid and phosphoric acid, the hydrolysis products of $POCl_3$ vapors, from both the reaction/distillation equipment and from transferring operations (for either process):

$$POCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_4$$

Like phosphorus trichloride, phosphorus oxychloride is extremely corrosive and is shipped in returnable nickel drums. Prior to reuse, these drums are thoroughly washed with water and steam cleaned. Some recent use has been made of non-returnable epoxy lined steel drums.

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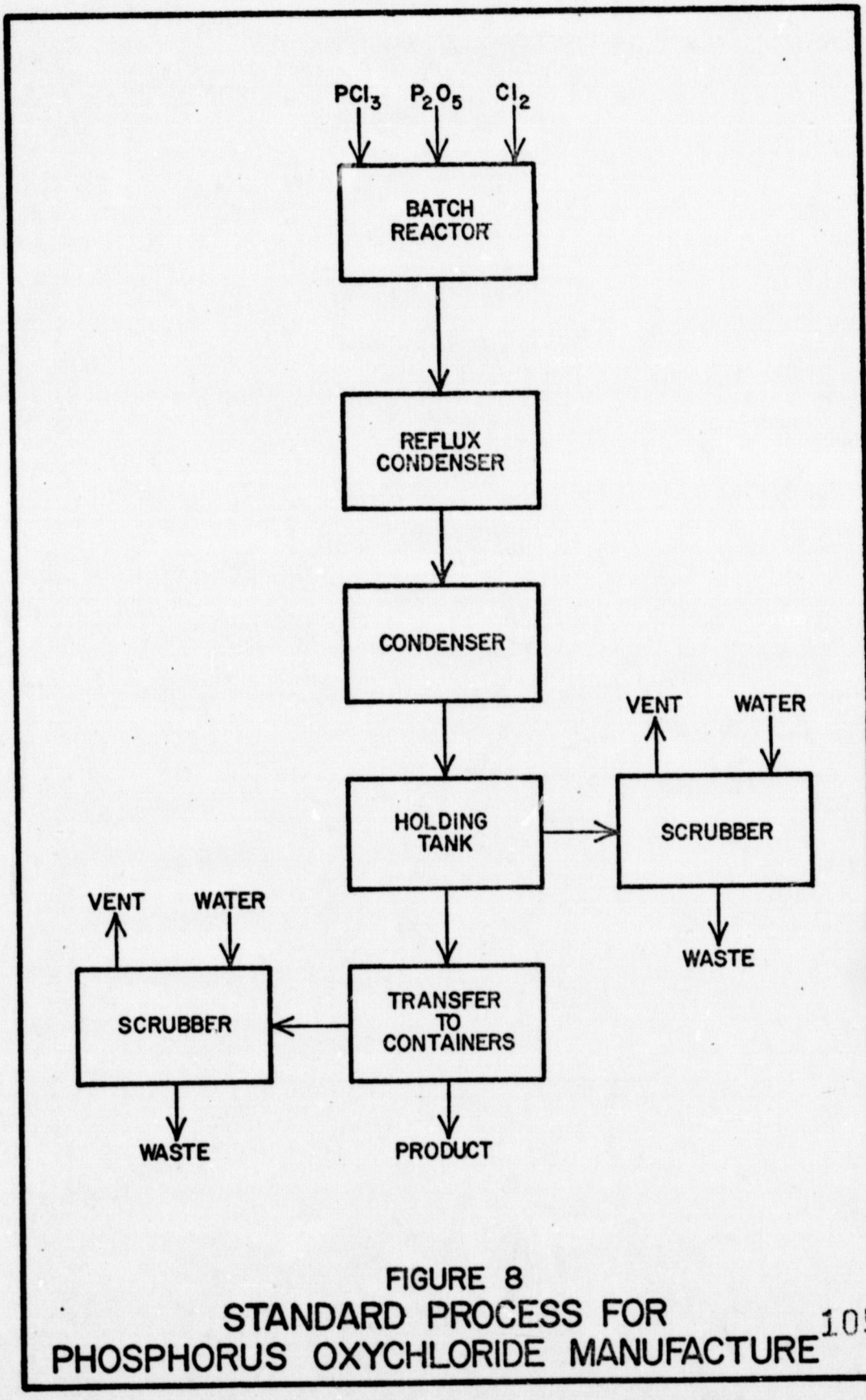


FIGURE 8
STANDARD PROCESS FOR
PHOSPHORUS OXYCHLORIDE MANUFACTURE

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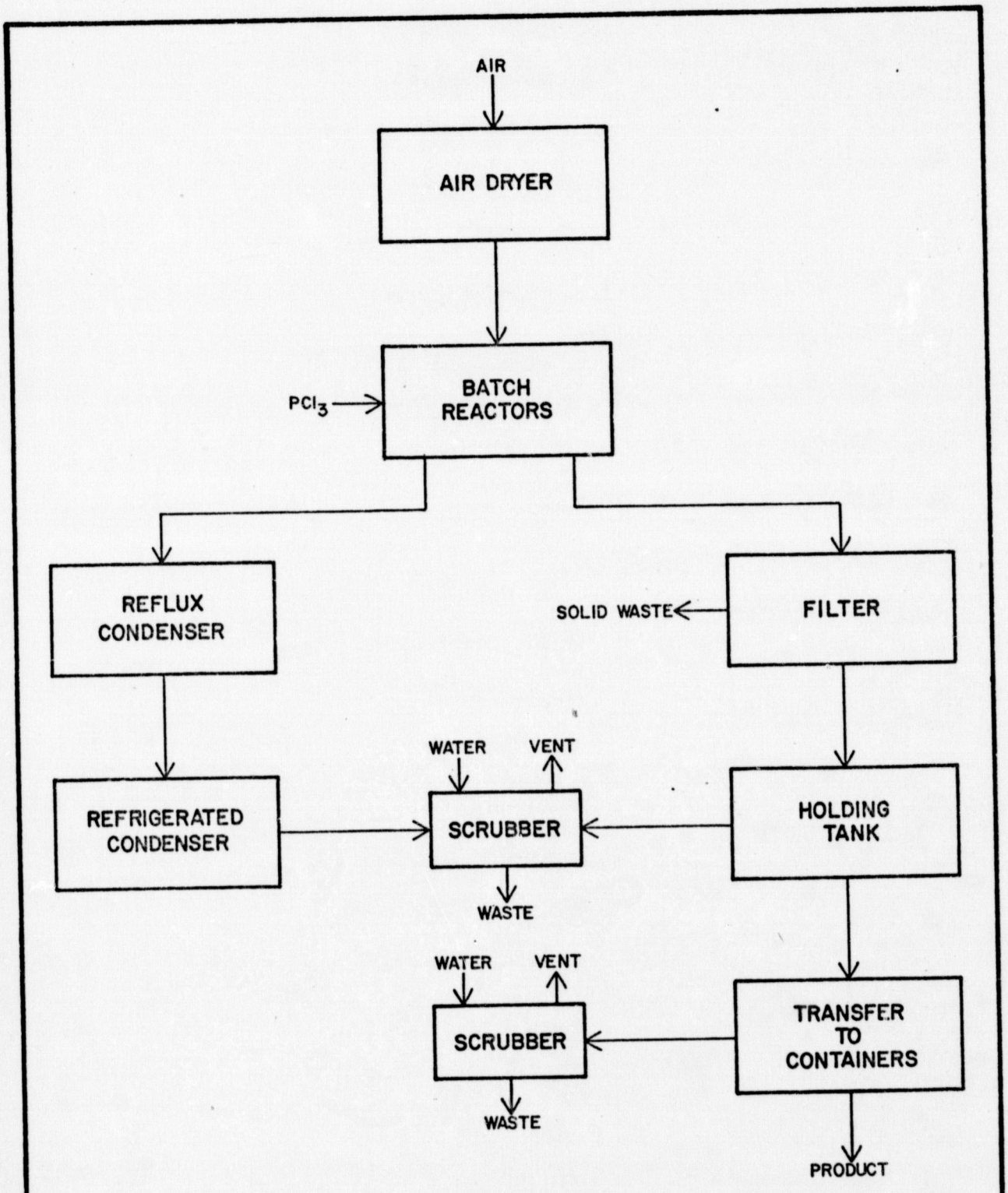


FIGURE 9

1056 ALTERNATE PROCESS FOR PHOSPHORUS OXYCHLORIDE MANUFACTURE

THE PHOSPHATE SEGMENT

Sodium Tripolyphosphate

Sodium tripolyphosphate is manufactured by the neutralization in mix tanks of phorphoric acid by soda ash or by caustic soda and soda ash, with the subsequent calcining of the dried mono and di-sodium phosphates crystals. Figure 10 is a flow diagram of the standard process. The sodium tripolyphosphate product is widely used in detergents and in water-softening applications. In the neutralization step, the amount of raw materials is measured and controlled to yield monosodium orthophosphate and disodium orthophosphate in a 1:2 mole ratio:

$$6H_3PO_4 + 5Na_2CO_3 \rightarrow 2NaH_2PO_4 + 4Na_2HPO_4 + 5H_2O + 5CO_2,$$

or

$$9H_3PO_4 + 5NaOH + 5Na_2CO_3 \rightarrow 3NaH_2PO_4 + 6Na_2HPO_4 + 10H_2O + 5CO_2$$

In either process variation, the final pH in the mix tank is very carefully adjusted by small additions of either phosphoric acid or caustic soda solution.

The mixture of sodium orthophosphates is spray-dried or drum dried and the solids calcined to produce the sodium tripolyphosphate:

$$NaH_2PO_4 + 2\ Na_2HPO_4 \rightarrow Na_5P_3O_{10} + 2\ H_2O$$

The product is then slowly cooled or tempered to preserve the condensed form of the phosphates. If the product is chilled too rapidly, it will revert to a mixture of the meta- and polyphosphates:

$$Na_5P_3O_{10} \rightarrow Na_3PO_3 + Na_2P_2O_7$$

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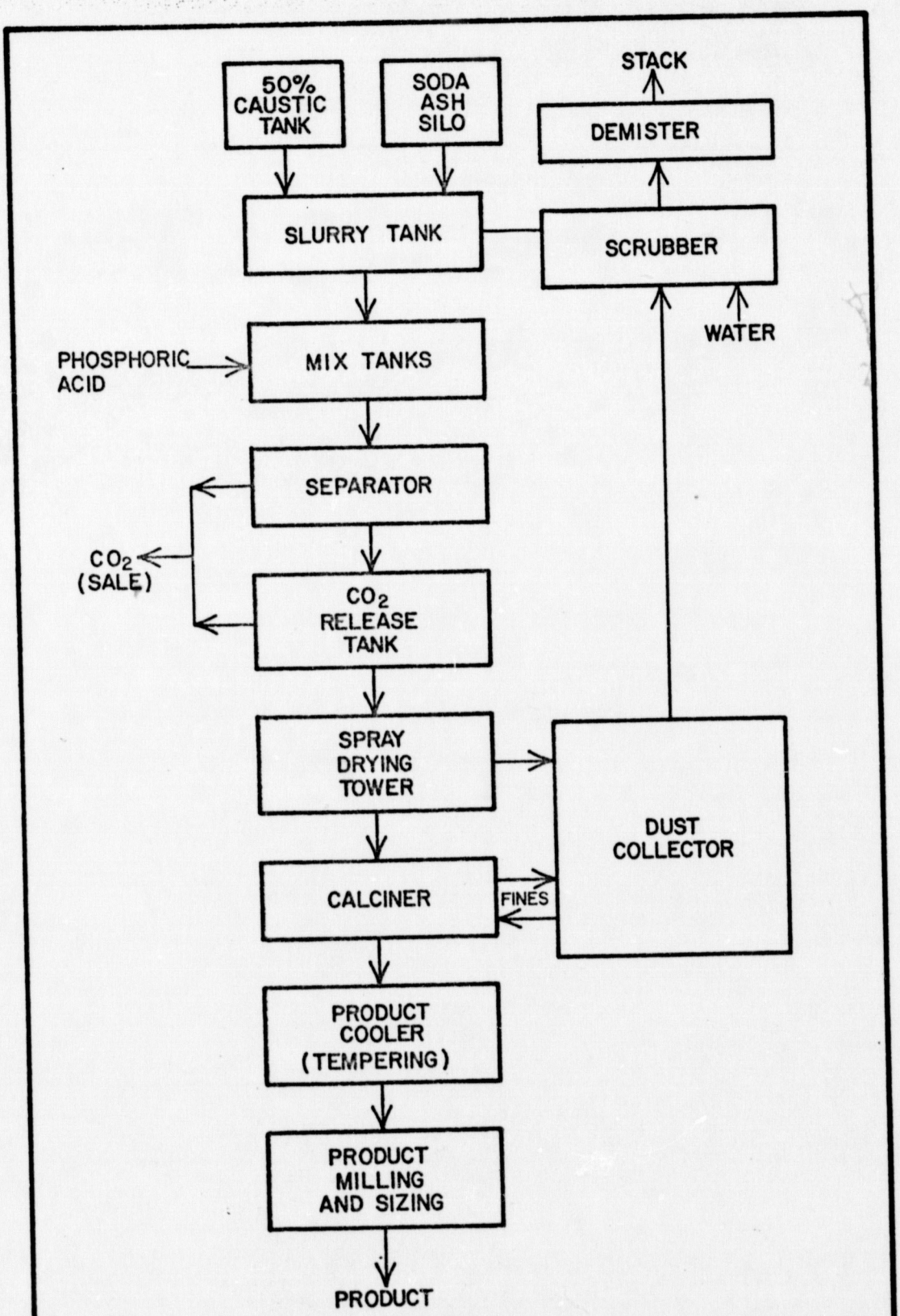


FIGURE 10

1058 STANDARD PROCESS FOR SODIUM TRIPOLYPHOSPHATE MANUFACTURE

Calcium Phosphates

The non-fertilizer calcium phosphates are made by the neutralization of phosphoric acid with lime. Although the reactions are chemically similar, the processes for manufacturing the different calcium phosphates differ substantially from one another in the amount and type of lime used and the amount of process water used (See Figures 11 and 12).

Relatively pure, food-grade monocalcium phosphate (MCP) is made in a stirred batch reactor from furnace acid and lime slurry:

$$2H_3PO_4 + Ca(OH)_2 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O + H_2O$$

An excess of phosphoric acid maintained during the batch addition cycle inhibits the formation of dicalcium phosphate. A minimum quantity of process water is used. The heat of reaction liberates some water as steam in the reactor, and the remaining water is evaporated in a vacuum dryer, a steam-heated drum dryer, or in a spray-dryer. The anhydrous MCP is produced by using CaO (quicklime) and in carrying out the reaction at 140°C (310°F) so that water is driven off as it is produced.

Relatively pure, food-grade tricalcium phosphate (TCP) is made in a similar manner to MCP, except that an excess of lime slurry maintained during the batch addition cycle inhibits formation of dicalcium phosphate:

$$2H_3PO_4 + 3Ca(OH)_2 \rightarrow Ca_3(PO_4)_2 + 6H_2O$$

Like MCP, the TCP is dried to prevent excessive product temperatures.

Relatively pure, food-grade dicalcium phosphate (DCP) is made in batch stirred reactors, but with much more process water than for either MCP or TCP:

$$H_3PO_4 + Ca(OH)_2 \rightarrow CaHPO_4 \cdot 2H_2O$$

The stoichiometry for DCP manufacture is critical; any excess H_3PO_4 during the batch addition cycle would result in some MCP and any excess $Ca(OH)_2$ would result in some TCP. The excess water in the DCP reactor is to ensure homogeneity so that the local stoichiometry is as balanced as the overall reactor stoichiometry.

As a result of the excess of water used, the reaction mixture is a pumpable slurry as opposed to the pasty consistency for MCP and TCP. This DCP is mechanically dewatered prior to drying.

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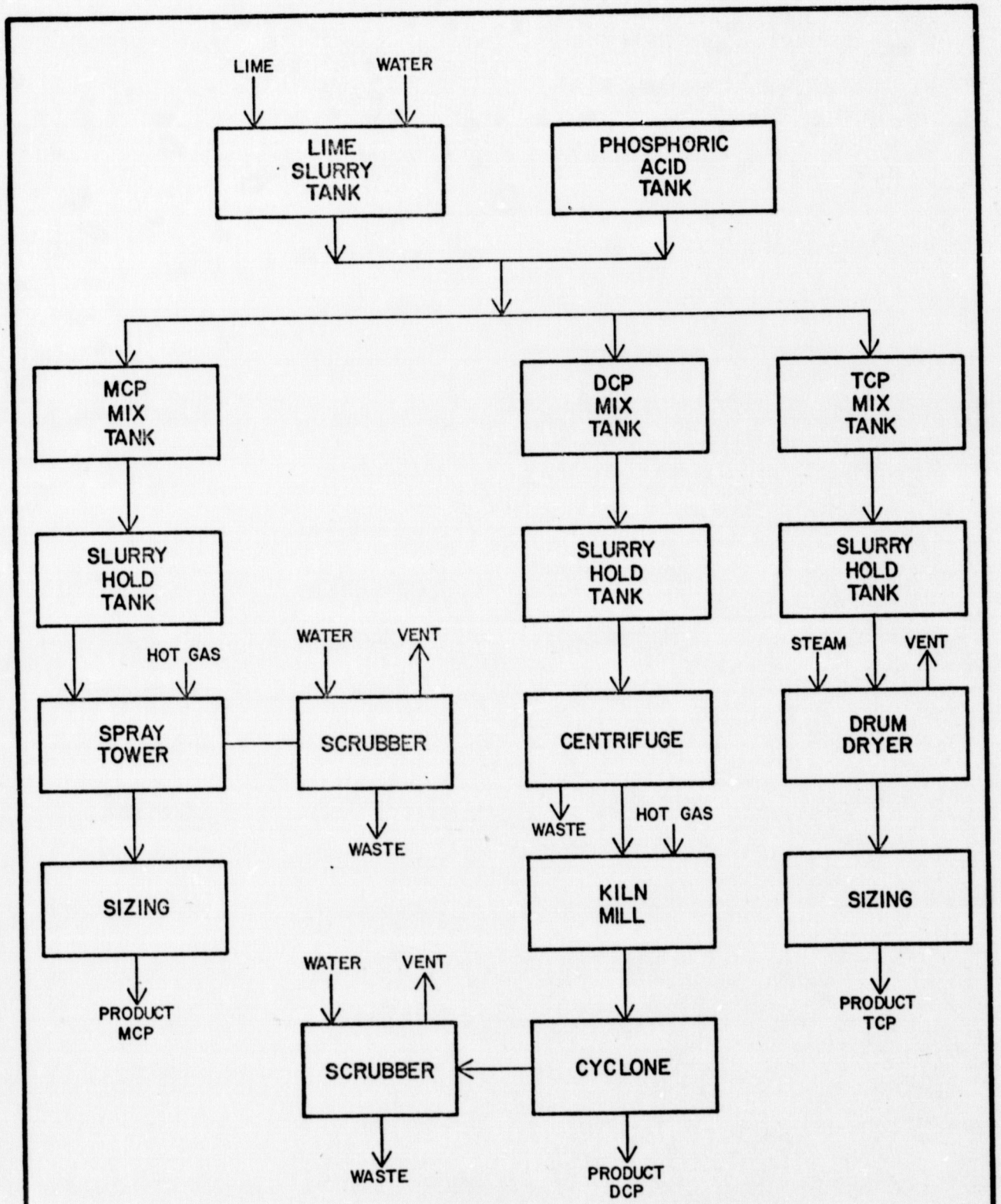


FIGURE 11
STANDARD PROCESS FOR
FOOD-GRADE CALCIUM PHOSPHATES

1000

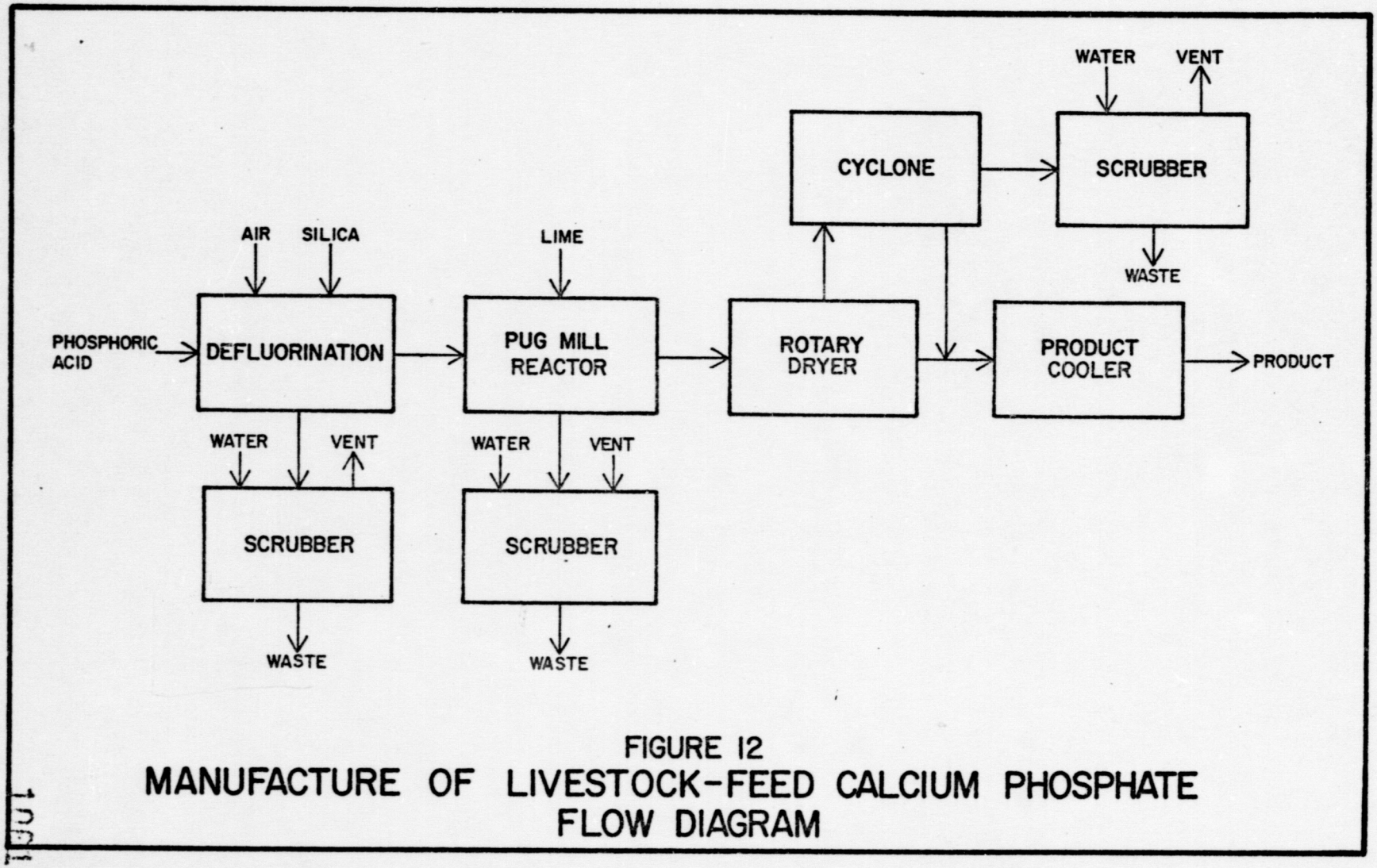


FIGURE 12
MANUFACTURE OF LIVESTOCK-FEED CALCIUM PHOSPHATE
FLOW DIAGRAM

Dicalcium phosphate (DCP) is also manufactured for livestock feed supplement use, with much lower specifications on product purity. Hence, the reaction can be conducted without excess water, since some MCP and/or TCP in the DCP product is perfectly tolerable. The pasty reaction product is normally dried in a rotary dryer. Powdered limestone, $CaCO_3$, may be used instead of lime. If quicklime is used, the drying step may be bypassed.

Another significant process difference is that non-food grade wet-process phosphoric acid is normally used for this product. The DCP plants defluorinate the acid unless this step was accomplished by the acid producer. Wet process phosphoric acid contains approximately one percent fluoride in various forms. The defluorination consists of treating the heated acid with finely-divided silica and steaming or aerating, which liberates silicon tetrafluoride gas:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Wet scrubbers then hydrolyze and collect this gas as fluosilicic acid and silicic acid:

$$3\ SiF_4 + 3H_2O \rightarrow 2H_2SiF_6 + H_2SiO_3$$

The hot defluorinated phosphoric acid is then charged to the reactor to make dicalcium phosphate.

SECTION IV

INDUSTRY CATEGORIZATION

INTRODUCTION

In developing effluent limitations guidelines and standards of performance for new sources for a given industry, a judgment must be made by the Environmental Protection Agency as to whether effluent limitations and standards are appropriate for different segments (subcategories) within the industry. The factors considered in determining whether such subcategories are justified for the phosphate category of point sources are:

wastes generated
treatability of waste waters
manufacturing process
raw materials
plant size and age
product
land availability
air pollution control equipment

WASTES GENERATED

Tables 7, 8, and 9 in section V compile the raw waste loads for the phosphate category. Suspended solids and dissolved phosphates are common raw waste water constituents for phosphorus, food grade calcium phosphates, and feed grade calcium phosphates. Dissolved solids are present in concentrations significantly above background for all the chemicals studied. Elemental phosphorus can be a waste water constituent common to all of the phosphate manufacturing industry if the phossy transport water is not returned to the phosphorus producing plant. Sulfates, fluorides, and alkalinity are constituents specific to phosphorus production. Furthermore, the amount of waste water (425,000 l/kkg of P_4) resulting from the production of phosphorus is several orders of magnitude greater than that generated from any of the other processes. The chemicals H_3PO_4, P_2O_5, P_2S_5, PCl_3, and $POCl_3$ commonly generate acidic wastes and phosphates.

TREATABILITY OF WASTE WATERS

Phosphorus production clearly stands alone on the basis of waste water treatability. The large amounts of waste water produced (425,000 l/kkg P_4) present special problems. It is commonly practiced within the industry to return phossy transport water to the phosphorus plant. Therefore, the problem of treating elemental phosphorus is only a phosphorus plant problem, or can be so handled, that it will be a problem unique to phosphorus plants.

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The chemicals H_3PO_4, P_2O_5, P_2S_5, PCl_3, and $POCl_3$ present similar treatability problems in that acidic wastes are encountered. PCl_3 and $POCl_3$ present more difficult problems because the resultant chloride ions are difficult to remove.

The calcium phosphates involve similar treatment problems (suspended solids and phosphates). Defluorination of animal feed grade calcium phosphates will produce fluoride wastes, but the proposed treatment schemes will handle this waste constituent.

MANUFACTURING PROCESS

Manufacturing process is the principal factor used to determine subcategories. Phosphorus production is an ore reduction process involving large electric furnaces and large amounts of raw material and slag. Ferrophosphorus is a byproduct in the phosphorus reaction and is always considered along with phosphorus when considering effluent quality.

The chemicals H_3PO_4, P_2O_5, PCl_3, and $POCl_3$ are all similar in that a gaseous phase intermediate or product is encountered somewhere in the reaction sequence. The synthesis of P_2S_5 resembles the above in that water and air must be completely absent in the whole or parts of the reaction sequence.

Sodium tripolyphosphate and the calcium phosphates are produced by the neutralization of phosphoric acid by alkaline slurries.

RAW MATERIALS

The following raw materials are used for each process:

Chemical	Raw Materials	
P_4 & Fe_2P	Phosphate Ore	Coke(C) SiO_2
H_3PO_4	P_4	O_2
P_2O_5	P_4	O_2
P_2S_5	P_4	S
PCl_3	P_4	Cl_2
$POCl_3$	PCl_3	Cl_2 (P_2O_5)
$Na_5P_3O_{10}$	H_3PO_4	Na_2CO_3 (NaOH)
Calcium Phosphates	H_3PO_4	$Ca(OH)_2$

When the nonphosphorus compounds are excluded, four subcategories become evident on the basis of raw material. The $POCl_3$ process is so like the PCl_3 process, however, that it is included in the latter subcategory.

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PLANT SIZE AND AGE

Plant size will not affect the quantities of wastes produced (kg per kkg of product) to such a degree that subcategorization would be warranted. The same basic production processes for each chemical are used throughout the phosphate industry. Plant age will not affect the quantities of wastes produced to the degree where subcategorization is warranted. Another point is that there are no really new plants, and consequently the situation does not exist where new technologies make older technologies obsolete. With respect to economics it is particularly difficult to access the effects of waste water treatment. These chemicals serve as raw materials or intermediates for other products produced by the same company. The theoretical profitability of a single plant may well not decide if operations are to continue at that site. With this in mind it would be difficult if not impossible to establish criteria based upon the economics of plant size or age for the purpose of subcategorization.

PRODUCT

The product does have some bearing on the waste water quality when the product or vapors from the product or intermediate come into contact with water. This topic has already been indirectly discussed under wastes generated. In summary, phosphorus production is associated with elemental phosphorus, phosphates, fluoride, suspended and dissolved solids. H_3PO_4, P_2O_5, P_2S_5, PCl_3, and $POCl_3$ result in phosphates, dissolved solids, and acids in the waste waters. $Na_2P_3O_{10}$ and the calcium phosphates result in phosphates, suspended and dissolved solids.

LAND AVAILABILITY

Removal of suspended solids from raw waste waters is most easily accomplished by use of large settling ponds. This will be the principle concern for land availability. However, the plants in this category are located in rural sites when the problem of land availability is minimized.

AIR POLLUTION CONTROL EQUIPMENT

All of the chemicals covered in this study use wet scrubbers or water systems in the process itself which amount to scrubbers. Therefore this is not a topic for subcategorization. Furthermore dry air pollution control equipment is recommended to either precede or replace wet scrubbers in order to reduce scrubber water contamination. Volitilization of hazardous substances such as fluorine from neutralization and settling ponds is insignificantly small.

SUBCATEGORIES

The factors that entered into the selection of subcategories are: wastes generated, treatability of waste waters, product, and particularly raw material and manufacturing process. Three subcategories were considered necessary for purposes of establishing effluent guidelines:

a. Phosphorus Production
    1. phosphorus
    2. ferrophosphorus
b. Phosphorus Consuming
    1. phosphoric acid (dry process)
    2. phosphorus pentoxide
    3. phosphorus pentasulfide
    4. phosphorus trichloride
    5. phosphorus oxychloride
c. Phosphate
    1. sodium tripolyphosphate
    2. Calcium phosphates
        i. animal feed grade
        ii. food grade

SECTION V

WATER USE AND WASTE CHARACTERIZATION

INTRODUCTION

With the background of manufacturing technology discussed in Section III, this Section discusses the specific water uses in the phosphate manufacturing industry and the raw wastes from this industry prior to control and/or treatment of these wastes. Both Section III and Section V are intended to be generally descriptive of the industry; i.e., they outline the standard manufacturing processes and the standard raw waste loads that are common to the great bulk of plants in the industry. It is not until Section VII, Control and Treatment Technology, and Section IX, Best Practicable Control Technology Currently Available, that distinctions are made (and quantitatively supported by independently-verified sampling data of plant effluents) within the industry, pointing out those notable plants which have already achieved significant reduction or total elimination of polluting discharges.

The discussion to follow this Section, therefore, should not be taken as implying that the raw waste loads quoted are always actual plant discharges. Rather, they are intended to describe the total waste management problem originally faced by any plant in the industry. In actuality, significant abatement steps have been taken by some plants within the industry. By fully explaining the total waste management problem (in terms of raw waste loads), the control and treatment steps can be later explained and evaluated.

SPECIFIC WATER USES

Water is primarily used in the phosphate manufacturing industry for eight principal purposes:

Non-contact Cooling Water
Process and Product Water
Transport Water
Contact Cooling or Heating Water
Atmospheric Seal Water
Scrubber Water
Auxiliary Process Water
Miscellaneous Uses

Non-Contact Cooling Water

Water used without contacting the reactants, such as in a tube-in-shell heat exchanger, is not contaminated with process effluent. If, however, the water contacts the reactants, then contamination of the water results and the waste load increases. Probably the single most

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important process waste control technique, particularly for subsequent treatment feasibility and economics, is segregation of non-contact cooling water from process water.

Non-contact cooling water is generally of two types in the industry. The first type is recycled cooling water which is cooled by cooling towers or spray ponds. The second type is once-through cooling water whose source is generally a river, lake or tidal estuary, and the water is returned to the same source from which it was taken.

The only waste effluent from the recycled water would be water treatment chemicals and the cooling tower blowdown which generally is discharged with the cooling water. The only waste effluent from the once-through cooling water would be water treatment chemicals which are generally discharged with the cooling water. The cooling tower blowdown may contain phosphates, nitrates, nitrites, sulfates and chromates. The water treatment chemicals may consist of alum, hydrated lime, and alkali metals such as sodium and potassium produced by ion exchange units. Regeneration of the ion exchange units is generally accomplished with sodium chloride or sulfuric acid, depending upon the type of unit employed in the plant.

Process and Product Water

The process or product water generally is that which comes in contact with the product and stays with the product as an integral part, such as the quenching, hydrolysis and dilution water used in phosphoric acid manufacture, or the water used as a reaction medium in food-grade dicalcium phosphate manufacture.

Transport Water

Water may be used for transporting reactants or products between unit operations. A pure example is in the use of water for transferring (by displacement) liquid phosphorus. Another example is the transfer of electrostatic precipitator dust in phosphorus manufacture as a slurry in water.

Since intimate contact between the process materials and transport water occurs, this water may generally contain dissolved or suspended materials and so is classified as process water.

Contact Cooling or Heating Water

This water comes under the general heading of process water because it comes in direct contact with process waters. A prime example is the large quantity of water used to quench the slag from phosphorus furnaces; another is the water used to condense the gaseous phosphorus after it is produced in the furnaces.

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Other direct contact cooling or heating water usage such as that for contact steam heating and/or drying, steam distillation, pump and furnace seals, etc., is generally of much lower volume than the barometric condenser water and is easier to treat for waste effluents.

Atmospheric Seal Water

Because some of the materials in this industry spontaneously ignite upon contact with the oxygen in air, the air is kept out of reaction vessels using a water seal. Liquid phosphorus is universally protected by storing under a water blanket. These seal waters are considered as process waters.

Scrubber Water

Throughout this industry, water scrubbers are used to remove process vapors and/or dusts from tail gases or from gaseous process streams. The used scrubber water is regarded as process water since direct and intimate contact has occurred; the resultant solution or suspension may contain impurities or may be too dilute a solution to reuse or recover and thus is discharged.

Auxiliary Process Water

This water is used in medium quantities by the typical plant for auxiliary operations such as ion exchange regenerants, makeup water to boilers with a resultant boiler blowdown, equipment washing, storage and shipping tank washing, and spill and leak washdown. The volume of waste water from these operations is generally low in quantity but highly concentrated in effluents.

Miscellaneous Water Uses

These water uses vary widely among the plants with general usage for floor washing and cleanup, safety showers and eye wash stations, sanitary uses, and storm run-off. The resultant streams are either non-contaminated or slightly contaminated with wastes. The general practice is to discharge such streams without treatment except for sanitary waste.

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PROCESS WASTE CHARACTERIZATION

The descriptions of the manufacturing processes in Section III, and the flow diagrams included in that Section, qualitatively discussed the sources of wastes. The following discussion is intended to quantify these waste streams both in quantity and in composition. These waste streams are the "raw" wastes prior to control or treatment (which is separately discussed in Section VII).

Aqueous wastes emanating from air pollution abatement equipment are considered as process wastes in this study.

The following sections quantify the raw process wastes in each segment of the industry. A discussion of the source, nature, and amount of these wastes for each segment is followed by a table summarizing the standard raw waste load.

Various plants in the industry differ significantly in the degree of process and cooling water recirculation. Hence, the waste water quantities and constituent concentrations quoted may be grossly different from plant-to-plant. However, the raw loads in kg per kkg of product (lb/ton) are dependent primarily upon the manufacturing processes and are therefore much more representative of the entire industry.

The Phosphorus Production Subcategory

The discussion of phosphorus manufacturing technology in Section III and the flow diagram of Figure 2, qualitatively pointed out the following streams emanating from the process (in addition, of course, to the phosphorus product stream):

By-products: Slag, Ferrophosphorus, and Carbon Monoxide
Non-contact Cooling Water
Electrostatic Precipitator Dust
Calciner Precipitator Dust
Calciner and Furnace Fume Scrubber Liquor
Phosphorus Condenser Liquor (Aqueous phase)
Phosphorus Sludge (or mud)
Slag Quench Liquor

The following sections discuss each of the above in quantitative detail, and identify which are typically returned to the process and which are classified as raw waste streams from the manufacturing operation.

By-product Streams

The by-products of the phosphorus manufacturing operation are:

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	kg/kkg	lb/ton
Ferrophosphorus	300	600
Slag ($CaSiO_3$)	8,900	17,800
CO gas	2,800	5,600

Both ferrophosphorus and slag are sold, and the carbon monoxide is either used to generate heat in the process or is otherwise burned on site. Hence, none of the above three materials is considered a waste.

The quench water used for the by-product slag is separately discussed as a waste stream.

The by-product ferrophosphorus is cast as it is tapped from the furnace and air-cooled. The solids are then broken up and shipped. No water is used specifically for ferrophosphorus, and there are no wastes accountable for ferrophosphorus manufacture.

Non-Contact Cooling Water

Phosphorus production facilities generate huge quantities of heat. The electrical power consumption is approximately 15,500 kwh/kkg (48 million Btu/ton). An additional 8,100 kwh/kkg (25 million Btu/ton) are generated by combustion of the by-product carbon monoxide. Some of this energy, 6,100 kwh/kkg (19 million Btu/ton), is absorbed in the endothermic furnace reaction, and some is absorbed by the endothermic calcining operation. Other portions of this energy are released to the atmosphere by burning of waste carbon monoxide (that not used for calcining) and by convection, radiation and evaporative losses from the equipment and process materials. Still other portions are absorbed by contact waters in the calcining and furnace from scrubbers, in the phosphorus condenser, and in the slag quenching operation.

After accounting for the above energy demands, a significant quantity of heat is absorbed by non-contact cooling water for the furnace shell, the crucible bottom, the fume hood, the tap holes, the electrode fixtures, the electrical transformer, and for any indirect phosphorus condensation. The quantity of this water is highly variable from plant-to-plant, and depends upon the furnace design, the furnace size and the degree of recirculation (through heat exchangers with other water streams or through cooling towers), whether or not cooling water is used in series for different requirements, the inlet temperature of the available cooling water, and the ambient air temperature. Plant 181 uses 325,000 liters/ kkg of product (78,000 gal/ton); Plant 159 uses 38,000 liters/ kkg (9,000 gal/ton); and TVA at Muscle Shoals, Alabama,(5) uses 130,000 l/kkg (31,000 gal/ton).

Electrostatic Precipitator Dust

The high-temperature electrostatic precipitator removes dusts from the furnace gases before these gases are condensed for recovery of phosphorus. These dusts may contain up to 50 percent P_2O_5, and therefore finds value either as a fertilizer for sale or for return to the process. In the latter case, it is transported to the ore blending head end of the plant. One TVA scheme slurries the dust for transport; the slurry is pumped to a settling pond, the settled solids are fed to the ore - blending unit, and the pond overflow is reused in the slurrying operation.

The quantity of precipitator dust is approximately 125 kg/kkg of product (250 lb/ton). Regardless of the method of sale or reuse, the precipitator dust is not a waste material to be disposed of from the plant.

Calciner Precipitator Dust

Dry dust collectors are used in the calcining operation, upstream of wet scrubbing systems. The dry fine dusts collected are recycled directly to the sizing and calcining operations. The collected and recycled fines may amount to as much as 30 percent of the net production from the nodulizing process.

There is no plant discharge of dry calciner precipitator dusts; therefore this is not a component of the plant's raw waste load.

Calciner and Furnace Fume Scrubber Liquor

Water scrubbers are used for air pollution abatement for the calciner exhaust stream (downstream of dry dust collection), for furnace fumes, for ore sizing dusts, for coke handling dusts, for raw material feeding operation dusts, and for furnace taphole (slag and ferrophosphorus) fumes. The scrubber liquor contains suspended solids (which are mainly SiO_2 and Fe_2O_3), some phosphates and sulfates as dissolved solids, and a large quantity of fluorides. To explain the presence of these fluorides in the scrubber liquor, Table 6 lists the quantities of materials in commercial phosphate rock. presented as pounds per ton of phosphorus ultimately produced after normalizing of 26 percent P_2O_5 content. From Table 6, the average quantity of F in ore is 275 kg/kkg of P_4 (550 lb/ton). Approximately 8 percent of this quantity of F, or 22 kg (44 lbs), is volatilized in the ore calcining operation, and is subsequently a constituent of the scrubber liquor.

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TABLE 6

Composition of Commercial Phosphate Rocks (12)

Expressed as kg per kkg (lb/ton) of Phosphorus Produced

Constituent	Florida Land Pebble Furnace Grade		Tennessee Brown Rock Furnace Grade		Western Phosphoric Acid Low Grade	
	kg/kkg	lb/ton	kg/kkg	lb/ton	kg/kkg	lb/ton
P_2O_5	2,600	5,200	2,600	5,200	2,600	5,200
CaO	3,800	7,600	3,550	7,100	3,150	6,300
MgO	35	70	75	150	190	380
Al_2O_3	125	250	1,230	2,460	810	1,620
Fe_2O_3	155	310	760	1,520	550	1,100
SiO_2	725	1,450	3,150	6,300	3,750	7,500
SO_3	215	430	50	100	260	520
F	305	610	270	540	245	490
CO_2	330	660	150	300	550	1,100
Organic Carbon	40	80	35	70	685	1,370
Na_2O	10	20	35	70	205	410
K_2O	10	20	50	100	135	270

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This scrubber liquor is highly acidic for three reasons: the sulfur (as SO_3) forms sulfuric acid: the P_2O_5 forms phosphoric acid; and the fluorine, which is released in the form of silicon tetrafluoride, forms fluosilicic acid and silicic acid upon hydrolysis.

The quantity of scrubber liquor wasted depends upon the degree of recirculation of this liquor from a sump back to the scrubbers. TVA at Muscle Shoals circulates approximately 21,000 l/kkg of product (5,000 lb/ton) with a portion bled off to control the composition. This scrubber liquor is of the following composition:

Constituent	Concentration, %
F	3.1
SiO_2	1.1
P_2O_5	0.2
Fe_2O_3	0.1
S	1.7

If the fluoride concentration of 3.1 percent is equated to a standard raw waste load (as previously discussed) of 22 kg/kkg (44 lb/ton), the quantities of other scrubber liquor components may be calculated:

Constituent	Raw Waste Load kg/kkg	lb/ton
F	22	44
SiO_2	8	16
P_2O_5	1.5	3
Fe_2O_3	0.5	1
S	12	24

The total $CaCO_3$ acidity of the scrubber liquor, calculated from the above constituent quantities, is 60 kg/kkg (120 lb/ton).

Other plants do not recirculate scrubber liquor; the volume wasted is much greater and the constituent concentrations are much smaller, but the raw waste loads (in kg/kkg of product) should be comparable. Plant 181 does not directly recirculate the liquor, and uses 300,000 l/kkg (71,000 gal/ton) for scrubbing.

Phosphorus Condenser Liquor

The furnace gases pass from the electrostatic dust precipitator to the phosphorus condenser, where a recirculating water spray condenses the product. The condenser liquor is maintained at approximately 60°C (140°F), high enough to prevent solidification of the phosphorus (freezing point 44°C (112°F)). This condenser liquor is "phossy water", essentially a colloidal dispersion of phosphorus in water, since the solubility at 20°C (68°F) is only 3.0 mg/l. Depending upon how intimate the water/phosphorus contact was, the phosphorus content of phossy water may be as high as several weight per cent.

The condenser liquor also contains constituents other than elemental phosphorus: fluoride, phosphate, and silica. Using the average F content of ore (from Table 6) of 275 kg/kkg, plus the estimate that 12 percent of the F in the ore volatilizes in the furance and is therefore equivalent to 33 kg/kkg (66 lb/ton), and by accounting for 6 kg of F per kkg (12 lbs/ ton) which is collected in the precipitator dust and in the phosphorus sludge ash; a raw waste load of F is derived of 27 kg/kkg (54 lb/ton) in the condenser liquor. This condenser liquor is not acidic despite the hydrolysis of P_2O_5 and SiF_4 to H_3PO_4, H_2SiF_6, and H_2SiO_3 because aqueous ammonia or caustic is added to prevent undue corrosion in the condenser.

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There are other sources of phossy water within the plant. Storage tanks for phosphorus have a water blanket, which is discharged upon phosphorus transfer. Railroad cars are cleaned by washing with water. Phosphorus may be purified by washing with water. Together, all sources of phossy water wastes amount to about 5,400 l/kkg (1,300 gal/ton), and at a concentration of 1,700 mg/l, the quantity of phosphorus wastes amount to about 9 kg/kkg produced (18 lb/ton), as reported by TVA.

At TVA, the condenser liquor is recirculated at the rate of 33,000 l/kkg (8,000 gal/ton). Other plants may differ significantly in the quantity of phossy water circulated, but the raw wastes (in kg/kkg of product) should be fairly uniform. For example, Plant 181, which does not directly recirculate its condenser water, uses 84,000 l/kkg (20,000 gal/ton), with an additional 17,000 l/kkg (4,000 gal/ton) for phosphorus handling and storage.

To calculate the raw waste loads of phosphate and silica in the condenser liquor, the following TVA recirculated-liquor composition was used:

Constituent	Concentration, %
F	8.3
P_2O_5	5.0
SiO_2	4.2

Equating 8.3 per cent F with the previously-derived 27 kg/kkg of F, the raw waste loads of P_2O_5 and SiO_2 become (respectively) 16.5 kg/kkg (33 lb/ton) and 13.5 kg/kkg (27 lb/ton).

Phosphorus Sludge

In addition to phossy water, the phosphorus condenser sump also collects phosphorus sludge, which is a colloidal suspension typically 10 per cent dust, 30 per cent water and 60 per cent phosphorus. The quantity of sludge formed is directly dependent upon the quantity of dust that escapes electrostatic precipitation; hence the very large investment made for highly efficient precipitators.

Using 125 kg of dust (per kkg of product) collected by the electrostatic precipitator, and assuming a 98 per cent collection efficiency, the dust reaching the condenser amounts to 2.5 kg/kkg (5 lb/ton). If all of this dust became part of the sludge, the sludge quantity would be 25 kg/kkg (50 lb/ton) of product, and it would contain 15 kg/kkg (30 lb/ton) of elemental phosphorus.

This sludge is then universally processed for recovery of phosphorus, typically by centrifugation. A 96 percent recovery has been reported, with the product (subsequently returned to the process) averaging 92 to

96 percent phosphorus. The remaining 4 per cent of the phosphorus in the sludge is burned in a phosphoric acid unit, so that no wastes emanate from the plant.

Other methods for processing the sludge which also result in no plant effluent include heating in a slowly rotating drum in an inert atmosphere to drive off phosphorus vapor, which is then condensed with a water spray into a sump. The solid residue obtained is completely free of elemental phosphorus and can be safely landfilled or recycled to the feed preparation section of the plant.

Slag Quenching Liquor

Slags from phosphorus furnaces are mainly SiO_2 and CaO, and would also contain Al_2O_3, K_2O, Na_2O, and MgO in amounts consistent with the initial ore composition. In addition to these oxides, phosphate rock may contain 0.1-0.2 kg/kkg (0.2-0.4 lb/ton) of uranium in the ore, and the radiation levels of both the slag and the quench waters must be appropriately noted. Other constituents of the slag presenting problems for quench water pollution control are fluoride and phosphate. Approximately 80 per cent of the original F in the phosphate rock, 220 kg/kkg of P_4 (440 lb/ton), referring to Table 6, winds up in the slag. About 2.7 per cent of the original P_2O_5 in the phosphate rock, 70 kg/kkg (140 lbs/ ton), wind up in the slag.

At Plant 181, approximately 24,600 l/kkg (5,900 gal/ton) may be used for quenching the slag, with the slag quench liquor having the following composition and raw waste loads:

Constituent	Concentration, mg/l	Raw Waste Load	
		kg/kkg P4	lb/ton P4
Total Suspended Solids	800	20	40
Total Dissolved Solids	1,700	42	85
Phosphates (as P)	12	0.3	0.6
Sulfate (as S)	1,000	25	50
Fe	14	0.35	0.7
F	170	4.5	9
Total Alkalinity	230	5.5	11

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TABLE 7

Summary of Raw Wastes from Phosphorus Manufacture

Note: Waste water Quantities and Constituent Concentrations are highly variable, depending upon degree of recirculation, but the raw waste loads should be representative.

	Calciner Scrubber Liquor	Phosphorus Condenser Plus Other Phossy Water	Slag Quenching Water	Composite Waste
Waste water Quantity,				
l/kkg	300,000	100,000	25,000	425,000
gal/ton	72,000	24,000	6,000	102,000
Raw Waste Load,				
kg/kkg				
TSS	8.5	13.5	20.5	42.5
P_4	-	9	-	9
PO_4	2	22	1	25
SO_4	36	-	75	111
F	22	27	4.5	53.5
Total Acidity	60	-	-	54.5
Total Alkalinity	-	-	5.5	-
Raw Waste Load,				
lb/ton				
TSS	17	27	41	85
P_4	-	18	-	18
PO_4	4	44	2	50
SO_4	72	-	150	222
F	44	54	9	107
Total Acidity	120	-	-	109
Total Alkalinity	-	-	11	-
Concentrations, mg/l				
TSS	28	135	820	100
P_4	-	90	-	21
PO_4	7	220	40	59
SO_4	120	-	3,000	260
F	73	270	180	126
Total Acidity	200	-	-	128
Total Alkalinity	-	-	220	-

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The Phosphorus Consuming Subcategory

No direct process aqueous wastes are generated in this segment of the industry. The raw wastes arise from phosphorus storage and transfer, from wet scrubbing of tail gases, from vessel cleaning, and from leaks and spills.

Phossy Water Wastes

Because phosphorus is transported and stored under a water blanket, phossy water is a raw waste material at phosphorus using plants as well as at phosphorus producing plants. The standard procedure when liquid phosphorus is transferred from a rail car to the using plant's storage tank is to pump the displaced phossy water from the storage tank back into the emptying rail car as practiced at Plants 037 and 192. Instead of being wasted at the phosphorus-using plant, the phossy water is shipped back to the phosphorus-producing facility for treatment and/or reuse. Therefore, standard raw phossy water wastes at the phosphorus-using plants are due to surges or to anomalies in the storage tank water level control system rather than to the direct wasting of all displaced water.

A more insidious source of phossy water may arise at phosphorus consuming plants. Should reactor contents containing phosphorus ever be dumped into a sewer as a result of operator error, emergency conditions or inadvertent leaks or spills, the phosphorus would remain at the low points in the sewer line generally as a solid (melting point 44°C (111°F)) and would contact all water flowing in that sewer from that time on. Since phosphorus burns when expcsed to air (autoignition temperature 93°C), there is general reluctance to clean it out; the common practice is to ensure a continuous water flow to prevent fire.

The typical phosphorus loss for phosphorus-consuming plants is 1 kg lost to phossy water per kkg consumed (2 lb/ton). Whenever phosphorus is tranferred by displacement, 580 liters of water are displaced per kkg of phosphorus (140 gal/ton). These values are equivalent to a phosphorus concentration of 1700 mg/l. For comparison, a typical phosphorus content in phossy water at a phosphorus-producing plant has also been reported at 1700 mg/l.

Phosphoric Acid Manufacture

The production of phosphoric acid by the "dry" process from elemental phosphorus consumes a total of about 380 liters of water per kkg of product (92 gal/ton) for both the hydration and the acid dilution steps. The cooling water requirements are typically 92,000 liters per kkg of product (22,000 gal/ton); but with recycle of cooling water, the makeup cooling water requirement is approximately 4,600 liters per kkg of product (1,100 gal/ton). There is no aqueous process waste from notable

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phosphoric acid Plants 003, 006, 042, and 075. However, despite good housekeeping at an notable plant, leaks or spills of phosphoric acid may account to an average of 1 kg/kkg (2 lb/ton), with a range of 0 to 2.5 kg/kkg (0 to 5 lb/ton).

Where food-grade phosphoric acid is produced, a standard raw waste of 0.1 kg/kkg (0.2 lb/ton) of arsenic sulfide is precipitated by addition of a soluble sulfide (H_2S, Na_2S, NaHS), and filtered out of the acid. An additional 0.75 kg/kkg (1.5 lb/ton) of filter-aid material may accompany the sulfide as a solid waste.

Phosphorus Pentoxide Manufacture

The waste water from the tail seals on the condensing towers typically contain 0.25 kg/kkg (0.5 lb/ton) of H_3PO_4 (100 per cent basis). Approximately 500 l/kkg (120 gal/ton) of water may be used, resulting in a concentration of 470 mg/l for the effluent bleed.

The inlet air dryer silica gel is regenerated often, but is renewed very infrequently (perhaps every ten years). The wasted material is typically landfilled.

Approximately 29,000 l/kkg (7,000 gal/ton) of non-contact cooling water is used.

Phosphorus Pentasulfide Manufacture

The water seals on the batch reactor vent lines accumulate a mixture of phosphorus mud and lower phosphorus sulfides. These seals are cleaned once a week, and the residue amount to 0.15 kg/kkg (0.3 lb/ton). This residue is hazardous and flammable, and is typically buried.

Should any batch be aborted (a rare occurrence) because of agitator failure, cast-iron pot failure or other reason, the material is disposed of by incineration.

The dust collected by a cyclone from the P_2S_5 crushing operation amounts to 1 kg/kkg (2 lb/ton).

The still pot for the vacuum distillation step accumulates impurities, which include carbon and iron sulfur compounds and glassy phosphates. Most important, the residues contain arsenic pentasulfide, which is higher-boiling than the corresponding phosphorus pentasulfide. Arsenic occurs naturally with phosphorus (they are both Group V-A elements) at a level of about 0.075 kg/kkg (0.15 lb/ton), of arsenic which is equivalent to 0.05 kg of As_2S_5 per kkg of product P_2S_5 (0.1 lb/ton). The entire still pot residue is about 0.5 kg/kkg (1 lb/ton). Periodically, these residues are removed and the solids are broken up and

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buried. Approximately 17,000 l/kkq (4,000 qal/ton) of non-contact cooling water is used.

In the casting of liquid P_2S_5, the fumes from burning liquid (molten P_2S_5 auto-ignited) are scrubbed. Typically, the scrubber water contains 1.25 kg of combined P_2O_5 and SO_2 per kkg of product P_2S_5 (2.5 lb/ton). Because both P_2O_5 and SO_2 are absorbed by a water scrubber only with difficulty, the water flow rate is high, 30,000 l/kkg (7,200 gal/ton). These values reduce the concentrations of PO_2^{-3} and SO_3^{-2} in the scrubber effluent of 17 and 34 mg/l (respectively). Much lower scrubber flow rates could be used should weak caustic or lime be used instead of water.

Phosphorus Trichloride Manufacture

The batch or semicontinuous reactor/stills accumulate residues which are periodically but infrequently removed. These residues contain arsenic trichloride, which is higher-boiling than the corresponding phosphorus trichloride. Arsenic occurs naturally with phosphorus (they are both Group V-A elements) at a level of about 0.075 kg/kkg (0.15 lb/ton) of arsenic, which is equivalent to 0.05 kg of $AsCl_3$ per kkg of product PCl_3 (0.1 lb/ton). This is about half the quantity of total residue in the stills (exclusive of residual PCl_3 from the last batch or run before shutdown).

The average non-contact cooling water requirement is 54,000 l/kkg (13,000 gal/ton).

Water scrubbers collect PCl_3 vapors from the reaction, the product distillation, the product storage, and the product transfer operations, and hydrolyze these vapors to HCl and to H_3PO_3 (which may subsequently be oxidized to H_3PO_4). The quantity of PCl_3 collected is highly dependent upon the efficiency of the upstream condensers, since PCl_3 is highly volatile:

Temp, °C	Temp, °F	PCl_3 Vapor Pressure, mm Hg (27)
20	68	99
40	104	235
60	140	690
76	169	760

At Plant 037, sufficient heat transfer area was provided in the condensers to limit the raw waste load to 3 kg of HCl plus 2.5 kg of H_3PO_3 per kkg of product PCl_3 (6 lbs and 5 lb/ton). Approximately 5,000 l/kkg (1,200 gal/ton) of scrubber water were used to collect these wastes. Other smaller waste quantities of HCl and H_3PO_3 generated from tank car and returnable container cleaning operations have been included in these quantities.

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These quantities are based upon the most reliable data available at Plant 037; overall material balances of product PCl_3 shipped vs. elemental phosphorus received. These data, validated over long periods of time for profitability purposes, show a total loss of phosphorus trichloride of 5 kg/kkg (10 lb/ton). An estimated breakdown of this loss is:

Transfer and Storage of Phosphorus,	1.0 kg/kkg (2 lb/ton)
Reactor/Still Residues,	0.1 kg/kkg (0.2 lb/ton)
Scrubber for Distillation Tail Gases,	2.5 kg/kkg (5 lb/ton)
Transfer of PCl_3,	1.0 kg/kkg (2 lb/ton)

Other than the estimated loss of elemental phosphorus and the reactor/still residues, the losses which become water-borne raw wastes amount to 3.5 kg/kkg (7 lb/ton). Upon hydrolysis, this stoichiometrically becomes 3 kg/kkg (6 lb/ton) of HCl plus 2.5 kg/kkg (5 lb/ton) of H_3PO_3. These material-balance data have been used because of their long-term confirmation. Direct measurements of waste water flow rates and of waste water constituent analysis were not relied upon in this case since accurate flow rate measurements were not possible in the existing plant configuration and since no statistically-meaningful analytical data had been collected.
The acid wastes from washing tank cars and tank trucks, and from washing used $POCl_3$ filter elements, are very small at present. Water use data taken from Plant 037, supplemented by independent analyses of the waste water, yielded the results in Table 8. Total raw waste generated in truck-loading, in tank-car cleaning, and in filter-element washing is 0.014 kg/kkg (0.028 lb/ton) of HCl plus 0.003 kg/kkg (0.007 lb/ton) of total phosphates.

TABLE 8

Minor Wastes from Plant 037 (PCl_3 and $POCl_3$)

		Truck-Loading Vent Scrubber	Tank Car Cleanout Water	Filter Element Washout Drum
Water Use:	l/kkg	8.8	10.5	0.46
	gal/ton	2.1	2.5	0.11
Constituent Analysis, mg/l:				
	Chloride	340	715	6,480
	Total PO_4	260	26	590
	Total Acidity	660	-	18,200
Raw Waste Load, kg/kkg:				
	Chloride	0.0030	0.0075	0.0030
	Total PO_4	0.0023	0.0003	0.0003
	Total Acidity	0.0058	--	0.0083
Raw Waste Load, lb/ton:				
	Chloride	0.006	0.015	0.006
	Total PO_4	0.005	0.001	0.001
	Total Acidity	0.012	--	0.017

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Phosphorus Oxychloride Manufacture

The water scrubber for the distillation operation in the standard process (using P_2O_5 and Cl_2) typically collects 1.5 kg of HCl (anhydrous basis) and 0.25 kg of H_3PO_4 (100 per cent basis) per kkg of product $POCl_3$ (3 lbs and 0.5 lb/ton), and the scrubber for $POCl_3$ transferring collects about 0.2 kg of HCl and 0.15 kg of H_3PO_4 per kkg of product (0.4 lb and 0.3 lb/ton). Allowing for small wastes from returnable container cleaning operations, the standard raw waste load is 2 kg of HCl and 0.5 kg of H_3PO_4 per kkg of product (4 lbs and 1 lb/ton). Approximately 2,500 l/kkg (600 gal/ton) of water are used, so that the raw waste concentrations are 800 mg/l HCl and 200 mg/l H_3PO_4.

The source of the above data on raw waste loads was Plant 147 records and plant personnel analysis of these records. An independent verification of these results was not judged valid since at this plant neither an accurate determination of wastewater flowrate nor the collection of a distinct waste water sample from each unit operation contributing to the waste load was practical; and since statistically-valid background data was not at hand.

These waste quantities for $POCl_3$ manufacture are somewhat smaller than for PCl_3 manufacture since $POCl_3$ is less volatile (boiling point 107°C). In the batch process, the refluxing liquid is all PCl_3 at the start, but becomes increasingly richer in $POCl_3$.

The air-oxidation process presents a much more difficult task for the reflux condenser, since the vapors are highly diluted with non-condensibles. However, with the use of refrigerated condensers, the measured raw waste load is no different for this process. At Plant 037, data collected over three months from the reactor/still scrubber for $POCl_3$ manufacture, which had an estimated flowrate of 1,800 l/kkg (430 gal/ ton), had average net values of:

Chloride	669 mg/l
$CaCO_3$ acidity	1,213 mg/l

These data reduce to a raw waste of 1.2 kg/kkg (2.4 lb/ton) of HCl plus 0.35 kg/kkg (0.7 lb/ton) of H_3PO_4; which are extremely close to the corresponding values for Plant 147.

Where product $POCl_3$ is filtered, the used filter elements are first washed to hydrolyze the residual $POCl_3$. Disposable elements are then landfilled. The quantity of filtered solids retained on the elements is only a very small fraction of the weight of the used element. The elements are washed in a 55-gallon drum, so that a very small quantity of waste water (and of acid wastes) is involved compared to the scrubber waste load. Although there is no continuous withdrawal of residues from

$POCl_3$ distillations, very little residue accumulates. Twice a year, this residue (mostly glassy phosphates) is washed out with hot water.

The non-contact cooling water requirement for $POCl_3$ manufacture by either the standard or the alternate method is approximately 50,000 l/kkg (12,000 gal/ton).

Variability of Raw Wastes from the Production of Phosphorus Trioxide and Phosphorus Oxychloride

The data below indicates the variability of concentrations in the raw waste load at Plant 037.

Date (1973)	$CaCO_3$ Acidity, mg/l	Chloride, mg/l
2/27	1170	560
2/28	1220	603
3/1	1720	822
4/19	850	447
4/23	480	305
4/24	950	532
4/25	1430	851
4/26	1250	589
4/27	1300	1035
4/30	1120	518
5/1	1470	1040
5/2	1690	716
5/3	280	773
5/4	1340	603
5/7	1810	1000
5/8	1220	574
5/9	1290	716
Mean	1217	687
Std. Deviation	384	208
Std. Deviation	384	208
95% Conf. Int. (Single Day)	+_814	+_441

In this case, there was no damping capacity; the acidity and chloride concentrations were closely coupled to the manufacturing process. The comparison of the 95% confidence intervals with the daily data show only one point of 17 (for acidity) and no points outside (for chloride).

Based on these very limited samples of data, it appears that the classical statistics may be applied, but with extreme caution.

For the above sets of data from Plant 037, a value of $(X + 3\sigma) / X$ might represent a maximum allowable daily reading as a multiple of the mean:

Parameter	$(X + 3\sigma)/X$
Acidity Concentration	1.95
Chloride Concentration	1.91

This maximum allowable value would be extremely liberal, since a Students "t" value of 3 is equivalent to less than one reading in 100 being unduly rejected. To be even more liberal (since the data base for this analysis is extremely skimpy), the maximum value from the above table will be assumed, so that the effluent limitation guideline for the manufacture of PCl_3 and $POCl_3$ should be a maximum daily value no greater than twice the mean (as represented by consecutive 30 day averages).

pH can be controlled much more closely than other parameters. Hence, it is recommended that the pH limitation be met at all times.

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TABLE 9

Summary of Raw Waste from Phosphorus-Concuming Plants

	H_3PO_4 (75%)	P_2O_5	P_2S_5	PCl_3	$POCl_3$
Phossy Water: P_4 conc, ppm	1,700	1,700	1,700	1,700	--
l/kkg P_4 consumed	580	580	580	580	--
kgP_4/kkg P_4 consumed	1	1	1	1	--
gal/ton P_4 consumed	140	140	140	140	--
lb /ton P_4 consumed	2	2	2	2	--
Process Water Wasted: l/kkg Pdt	--	500	30,000	5,000	2,500
gal/ton Pdt	--	120	7,200	1,200	600
Raw Waste Load, kg/kkg Pdt:					
HCl	--	--	--	3	2
H_2SO_3	--	--	1	--	--
$H_3PO_3 + H_3PO_4$	1	0.25	0.5	2.5	0.5
Raw Waste Load, lb /ton Pdt:					
HCl	--	--	--	6	4
H_2SO_3	--	--	2	--	--
$H_3PO_3 + H_3PO_4$	2	0.5	1	5	1
Concentrations, mg/l: HCl	--	--	--	600	800
H_2SO_3	--	--	34	--	--
$H_3PO_3 + H_3PO_4$	High	470	17	500	200
Process Water Consumed: l/kkg Pdt.	380	--	--	--	--
gal/ton Pdt	92	--	--	--	--
Cooling Water Used: l/kkg Pdt	91,000	29,000	16,600	54,000	50,000
gal/ton Pdt	22,000	7,000	4,000	13,000	12,000
Solid Wastes, kg/kkg Pdt:					
As Compounds	0.1	--	0.05	0.05	--
Total Residues	--	--	0.7	0.05	<0.05
Solid Wastes, lb /ton Pdt:					
As Compounds	0.2	--	0.1	0.1	--
Total Residues	--	--	1.4	0.1	<0.1

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The Phosphate Subcategory

The aqueous wastes from this segment of the industry arise from the use of wet dust scrubbing equipment for the finely divided solid products, and from processes which use excess process water which may become a waste stream.

Sodium Tripolyphosphate Manufacture

Exemplary Plants 006, 042, and 119 have no process wastes. The dust collected from the spray dryer gaseous effluent stream is added to the spray dryer solid product stream. The water used for subsequent scrubbing of this gas stream from the spray dryer is then recycled to the mix area and is used as process water in the neutralization step. The cooling air used for the product tempering is vented into the spray dryer vent line upstream of the scrubbing operation.

The neutralization step requires a total of 1,040 l/ kkg (250 gal/ton), of which 290 l/kkg (70 gal/ton) are recycled from the scrubber. Make-up water, 750 l/kkg (180 gal/ton), are added since water is evaporated in the product drying step. The makeup water is softened, and regeneration of the softener combined with boiler and cooling tower blowdowns amounts to 210 l/kkg (50 gal/ton); 70 per cent of which is from water treatment regeneration and 30 per cent from blowdowns. These blowdown wastes typically contain 1,500 mg/l of dissolved chlorides.

Calcium Phosphates

The raw aqueous wastes from the manufacture of food-grade calcium phosphates are from two primary and approximately equal sources: the centrate or filtrate from dewatering of the dicalcium phosphate slurry, and the effluent from wet scrubbers which collect airborne solids from product drying operations.
Both of these sources contain suspended, finely-divided calcium phosphate solids. It is normal practice in an integrated plant to partially recycle the scrubber water and to partially utilize the DCP centrate or filtrate as makeup scrubber water, as at Plant 003.The total raw wastes from this system are typically 4,200 l/kkg (1,000 gal/ton) containing 100 kg/kkg (200 lb/ton) of solids (a concentration of 2.4 per cent). An additional 30 kg/kkg (60 lb/ton) of dissolved solids (0.7 per cent of this waste stream) originates from phosphoric acid mists in the scrubbers and from excess phosphoric acid in the reaction liquid.

For non-food grade dicalcium phosphate plants, the water scrubbers which collect airborne solids normally operate at partial recycle. Since there is no waste from a dewatering operation, and since dry dust collection typically precedes wet scrubbing, the raw wastes are considerably

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smaller than for the food-grade operation. Dry dust collection is typical since only one or two products are made, so that the collected solids may be added directly to the product stream without extensive segregation. Moreover, since purity requirements are considerably less severe, the product stream can tolerate such additions. With the above measures, the wet scrubber wastes are typically 420 l/kkg (100 gal/ton) containing 22.5 kg/kkg (45 lb/ton) of suspended solids (a concentration of 5 per cent) plus 4 kg/kkg (8 lb/ton) of dissolved phosphates from acid mists (0.7 per cent). At the notable Plant 182, this bleed stream from the wet scrubber recirculation system is charged directly to the neutralization reactor; hence, this plant had no discharge whatever. As an added feature, this notable plant used cooling water blowdown as makeup to the airborne-solids scrubbing system, thereby eliminating all aqueous discharges (except for the effluent from regeneration of the water softener).

For the non-food grade plants, however, acid defluorination is an additional source of raw wastes (unless already-defluorinated acid is delivered to the plant). Wet-process phosphoric acid (54 per cent P_2O_5) contains approximately one per cent fluorine. Upon silica treatment, 13.5 kg per kkg of acid (27 lbs/ ton), or 10.5 kg of silicon tetrafluoride product dicalcium phosphate dihydrate (21 lb/ton), are liberated. When hydrolyzed in the acid scrubber, the raw waste contains 12 kg/kkg product (24 lb/ton) of combined fluosilicic acid (H_2SiF_6), hydrofluoric acid (HF) and silicic acid (H_2SiO_3). These raw wastes are contained in a scrubber water flow of 6,300 liters/ kkg (1,500 gal/ton), so that the combined concentration of fluosilicic acid, hydrofluoric acid and silicic acid is 1,900 mg/l. For any plant manufacturing calcium phosphates of any grade, non-contact cooling water is used in reactors and/or in dried product coolers.

Other possible sources of aqueous wastes are from regeneration of water softeners and from storm water runoff (all exterior surfaces of calcium phosphate plants become coated with fine lime and/or phosphate dusts).

In dry-product plants, a significant housecleaning effort must be continually maintained. In non-food grade calcium phosphate plants, the dry product sweepings (from dust, spills, etc) are added to the process stream. In food-grade plants, however, the sweepings (consisting of lime. lime grit, and calcium phosphates) are wasted. Typically, this solid waste amounts to 10 kg/kkg (20 lb/ton).

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TABLE 10

Summary of Raw Wastes from Phosphate Plants

	Sodium Tripoly-Phosphate	Food Grade Calcium Phosphates		Animal Feed Calcium Phosphates	
		Dewatering	Solids Scrubbing	Acid Defluorination	Solids Scrubbing
Process Water Wasted:					
l/kkg Pdt	0	2,100	2,100	6,300	420
gal/ton Pdt	0	500	500	1,500	100
Raw Waste Load, kg/kkg Pdt:					
TSS	-	50	50	-	22.5
Dissolved PO_4	-	15	15	-	4
HF, H_2SiF_6, H_2SiO_3	-	-	-	12	-
Raw Waste Load, lb/ton Pdt:					
TSS	-	100	100	-	45
Dissolved P_4	-	30	30	-	8
HF, H_2SiF_6, H_2SiO_3	-	-	-	24	-
Concentrations, mg/l:					
TSS	-	24,000	24,000	-	54,000
Dissolved PO_4	-	7,000	7,000	-	7,000
HF, H_2SiF_6, H_2SiO_3	-	-	-	1,900	-
TDS, mg/l	-	7,000	7,000	1,900	7,000
Solid Wastes:					
kg/kkg Pdt	0	10		-	-
lb/ton Pdt	0	20		-	-

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SECTION VI

SELECTION OF POLLUTION PARAMETERS

INTRODUCTION

Section V of this report quantitatively discussed the raw wastes generated in the phosphate manufacturing industry. The following were identified as being constituents of the industry's process waste waters:

Suspended Inorganic Solids
Dissolved Phosphates or Phosphites
Dissolved Sulfates or Sulfites
Dissolved Fluorides or Fluorosilicates
Dissolved Chlorides
Total Dissolved Solids
Acidity or low pH
Heat (High Temperature)
Elemental Phosphorus
Arsenic Compounds
Vanadium, cadmium, radium and uranium

The following discussion examines each of the above constituents and their impact upon receiving waterways from a chemical, a physical and a biological viewpoint. Additional, constituents such as hexavalent chromium, iron, alkalinity, and hardness, which are of typical concern whenever blowdowns from cooling towers, boilers and water treatment facilities are involved, are noted here but are not discussed in detail in this study (which deals more specifically with the process wastes of the phosphate industry).

SUSPENDED INORGANIC SOLIDS

Suspended solids discharged into receiving waters adversely impair navigation, recreation, water supply and fish propagation water uses. Navigation may be impaired as a result of sedimentation in quiescent regions in the stream bed. Recreational and water supply uses would be impaired as a result of turbidity of the water. The fish population suffers from loss of suitable breeding areas, loss of food chain organisms because of change in benthic characteristics, fish kills from excessive turbidity, and reduction of light penetration into the streams.

Suspended solids affect fisheries directly by covering the bottom of a stream with a blanket of material which kills out the bottom fauna, directly depriving the fish of a considerable part of their food (which lies at the bottom), or indirectly by eliminating species in the food chain. In addition, portions of the bottom, usually in the shallower

parts of the stream, provide nesting sites and spawning grounds for certain species.

The suspended solids directly affect fish through mechanical and abrasive action which clogs or otherwise injures the gills and respiratory structures. Although normal healthy fish secrete mucus to wash away suspended solids as they lodge on gills and other exposed parts, the synergistic action of other pollutants such as small amounts of acid wastes greatly augments the abrasion by solids by inhibiting the normal flow of mucus.

Indirectly, suspended solids affect fisheries by effectively screening out the light necessary to species of flora which may be important parts of the food chain. Also indirectly, but none the less effectively, solids which settle at the bottom trap organic wastes which might otherwise be dispersed, thereby increasing the oxygen demand at the bottom of the stream with disastrous results to the bottom fauna.

Of special concern in the phosphate industry is that much of the suspended solids in the raw wastes are calcium phosphates. It has recently been shown that calcium phosphates deposited in bottom muds of lakes are not inert solids, but are indeed available for uptake by the lake waters, and are a prime source of nutrients for algae blooms and a prime cause for lake eutrophication.

DISSOLVED PHOSPHATES AND PHOSPHITES

Phosphites are oxidized to phosphates in streams, exerting a chemical oxygen demand upon the streams.

The controversy over the nutrient and eutrophication effects of phosphates has received much attention in recent years, resulting from the phosphate constituent in domestic wastewater. The average concentration in domestic waste water is 30 mg/l (as PO_4); and the domestic waste quantities are about 1.6 kg (3.5 lbs) per capita per year, one-third of which are from human excretions and two-thirds from synthetic detergents. Runoff of synthetic fertilizers also contribute heavily to phosphate pollution of surface waters. For the purpose of this study, it appears sufficient to rely for guidance upon the massive effort and expenditure to remove phosphates from domestic waste water to come to the conclusion that dissolved phosphates from the industry under study are indeed a pollution parameter.

The natural concentration of phosphates in sea water is 0.7 to 1.4 mg/l.

DISSOLVED SULFATES OR SULFITES

Sulfites are oxidized to sulfates in streams, exerting a chemical oxygen demand upon the streams.

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Sulfates are not particularly harmful, but are a major constituent of the total dissolved solids in waste waters from this industry (and are discussed separately as such).

DISSOLVED FLUORIDES AND FLUOROSILICATES

Fluosilicic acid and its salts are highly deleterious materials. They also decompose to form fluorides. Hydrolysis causes fluosilicates to form gelatinous precipitates which are difficult to settle and dewater in treatment operations.

Fluorides are present in natural waters in concentrations less than 1 mg/l, and are widely used as drinking water additives in concentrations of a few mg/l for beneficial dental effects. However, at higher concentrations than 7 or 8 mg/l, fluorides have caused severe damage to bone structures. Fluorosis from airborne fluorides has been documented in cattle and in humans in the proximity of phosphate-rock mining operations.

Fluorides and fluorosilicates are definitely harmful materials, and can be identified as pollution parameters for the purposes of this study.

DISSOLVED CHLORIDES

Dissolved chlorides are a major constituent of the total dissolved solids in waste waters from this industry (and are discussed separately as such).

Sodium and calcium chlorides are found naturally in unpolluted waters, but are harmful to fish in high concentrations.

The natural salinity of river water in the Chesapeake Estuary is 9.5 to 11.0 mg/l of chloride; and the natural salinity of ocean water is 7,000 to 10,300 mg/l of chloride.

TOTAL DISSOLVED SOLIDS

Unpolluted natural waters contain small quantities of dissolved carbonates, chlorides, phosphates, sulfates and nitrates. All of the substances in solution in river water exert osmotic pressure on the aquatic organisms, and many of these substances are physiologically active, so that the organisms have become adapted to this salt complex. Most aquatic species will tolerate changes of considerable magnitude in the relative amounts of these salts provided the total dissolved solids remains constant.

The specific conductance, a direct measure of dissolved inorganic solids, lies between 150 and 500 umhos/cm in inland streams and rivers which support good, mixed fish faunas. In the Western plains and desert

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reas, natural quantities of dissolved solids are higher, with specific conductance ranging to 2,000 umhos/cm. The blood of fresh-water fish contains approximately 7,000 mg/l of dissolved salts (mainly NaCl). If the total dissolved solids in the external medium exceed this 7,000 mg/l by much, water will be withdrawn by osmosis from the gills of fish and from other delicate external organs of various species of aquatic life with lethal effects.

ACIDITY OR LOW pH

cidity, or low pH, kills fish through the precipitation and coagulation of the mucus on the gills and by the coagulation of the gill membranes themselves (specifically the proteins in the membranes). This precipitation and coagulation proceeds rapidly below a pH of 4.5; but species unprotected by mucus (such as Daphnia magna) are killed below a pH of 5.5

typical State water quality standard (that of Maryland) specifies a pH of 6.0 to 8.5 regardless of water use.

EAT (HIGH TEMPERATURE)

The impact of high water temperatures takes several forms which may also act synergistically:

(a) Alteration of the physical properties of water.
(b) Decrease in the solubility of oxygen upon which most aquatic organisms depend.
(c) Increase in the rate of chemical and biochemical reactions, particularly in the oxidation of organic wastes (thereby decreasing the level of dissolved oxygen).
(d) At sufficiently high temperatures, organisms are killed directly.
(e) Physiological processes such as reproduction, development and metabolism are temperature-dependent.
(f) Temperature anomalies can block the passage of anadromous fish, greatly reducing future populations.

Most fish are poikilothermal animals whose body temperature follows changes in environmental temperatures rapidly and precisely. The tolerance of fish to high temperatures is dependent upon the normal temperature to which the fish are acclimated and to the abruptness of temperature changes (both temporally and spatially). In general, however, the upper temperature limits for fish survival are in the range of 25 to 35°C (75 to 95°F).

A typical State water quality standard (that of Maryland) specifies the following with respect to heat rise regardless of water use:

Type of Water	Natural Temp, °F	Max. Temp Rise, °F	Maximum Temp, °F
Tidal	50	20	60
	50	10	90
Non-Tidal	50	20	60
	50	10	93

ELEMENTAL PHOSPHORUS

Elemental phosphorus has been identified as an extremely harmful material in very small amounts. The lethal dose for humans is 100 mg and the chronic dose is 1 mg/day. Ingestion of elemental phosphorus by the human body causes bone and liver damage.

ARSENIC COMPOUNDS

The dangerous properties of arsenic compounds in very small amounts is well known. The Federal Water Quality Administration presented a summary of the hazards of arsenic. The U.S. Public Health Service Drinking Water Standards set a maximum concentration of 0.05 mg/l, with a recommended limit of 0.01 mg/l. There is a continuing controversy over the health hazards of minute quantities of arsenic either naturally entering the ground or surface waters; and particularly over the arsenic that occurs naturally in phosphates (at a level of As:P of 75 mg/l) and is subsequently discharged into municipal waste water.

VANADIUM, CADMIUM, RADIUM AND URANIUM

Phosphate rock ore does contain trace amounts of one or more of these elements. These elements are chemically and/or radioactively harmful as detailed in Reference 72, but are not in such concentrations as to cause a serious health problem.

CONCLUSION

In view of the data presented above, it is judged that all of the mentioned waste constituents generated in the phosphate industry be identified as pollution parameters as defined in the Federal Water Pollution Control Act Amendments of 1972.

In the paragraphs above, the harmful characteristics are given of all the parameters that are encountered in the phosphate manufacturing point source category. Table 11 summarizes the parameters found for each chemical. The chemicals PCl_3 and $POCl_3$ require further consideration.

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TABLE 11

WASTE WATER CONSTITUENTS OF PHOSPHATE CATEGORY

Chemical	Parameter										
	TSS	PO_4 PO_3	SO_4 SO_3	F SiF_6	Cl	TDS	low pH	Heat	P_4	As	V, Cd, Ra, U
P_4 & Fe_2P	0	0	0	0		0	0	0	0	0	0
H_3PO_4		0				0	0	0	0	0	
P_2O_5		0				0	0	0	0		
P_2S_5		0	0			0	0	0	0	0	
PCl_3	X	0			0	X	X	0	0	0	
$POCl_3$	X	0			0	X	X	0	0	0	
$Na_5P_3O_{10}$		0				0	0	0	0		
$CaHPO_4$ (feed grade)	0	0		0		0	0	0	0		
$CaHPO_4$ (food grade)	0	0				0	0	0	0		

Althouqh many parameters appear in the waste streams from these plants only those primary parameters siqnified by "x" need be used to set effluent standards.

The remainina parameters for PCl_3 and $POCl_3$ siqnified by zeros are adequately treated if the primary parameters are so treated. Special consideration for these two chemicals is necessary since they are the only exceptions to the proposed guidelines (no discharqe of process waste water pollutants) for this cateqory.

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SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

INTRODUCTION

Section V of this report quantitatively discussed the specific water uses in the phosphate industry and the raw wastes from this industry prior to control and/or treatment of these wastes. Section VI identified the constituents of the raw wastes which are classified as pollutants. Table 11 summarizes the pollutant constituents found as raw wastes in each of the three segments of the industry:

Two major observations may be made from table 11:

1. Classical sanitary engineering practices that treat effluents containing organic material or that are aimed at reducing biological oxygen demand are inapplicable to the phosphate manufacturing industry, where such pollutant constituents are usually very low and not a significant factor. Hence, control and treatment of the wastes in this industry are of the chemical and chemical engineering variety, and include neutralization, pH control, precipitation, ionic reactions, filtration, centrifugation, ion exchange, demineralization, evaporation and drying.

2. A limited number of pollutant constituents characterizes the entire industry, crossing the lines between segments of the industry. Hence, the control and treatment techniques should be similar throughout the industry.

In this section of the report, the control and treatment technology is discussed in considerable detail. Much of this discussion is based upon observed actual abatement practice in the industry; the accomplishments of independently-verified sampling data of plant effluents.

IN-PROCESS CONTROLS

Control of the wastes includes in-process abatement measures, monitoring techniques, safety practices, housekeeping, containment provisions and segregation practices.

Segregation of Water Streams

Probably the most important waste control technique, particularly for subsequent treatment feasibility and economics, is segregation.

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Incoming pure water picks up contaminants from various uses and sources including:

1. non-contact cooling water
2. contact cooling water
3. process water
4. washings, leaks and spills
5. incoming water treatments
6. cooling tower blowdowns
7. boiler blowdowns

If wastes from these sources are segregated logically, their treatment and disposal may sometimes be eliminated entirely through use in other processes or recycle. In many instances, the treatment costs, complexity and energy requirements may be significantly reduced. Unfortunately, it is a common practice today to blend small, heavily contaminated streams with large non-contaminated streams such as cooling water effluents. Once this has been allowed to happen, treatment costs, energy requirements for these treatments, and the efficient use of water resources have all been compromised.

In general, plant effluents can be segregated into:

1. Non-contaminated Cooling Water. Except for leaks, non contact water has no waste pickup. It is usually high volume.

2. Process Water. Usually contaminated but often small volume.

3. Auxiliary Streams. Ion exchange regenerants, cooling tower blowdowns, boiler blowdowns, leaks, washings - low volume but often highly contaminated.

Although situations vary, the basic segregation principle is don't mix large uncontaminated cooling water streams with a smaller contaminated process and auxiliary streams prior to full treatment and/or disposal. It is almost always easier and more economical to treat and dispose of the small volumes of waste effluents - capital costs, energy requirements, and operating costs are all lower.

In the phosphorus chemicals industry, many plants have accomplished the desired segregation of water streams, often by a painstaking rerouting of sewer lines which have existed for many years. Among these plants which are notable in this respect are Plants 003, 037, 042, 075, and 182.

Recycle of Scrubber Water

The widespread use of water for scrubbing of tail gases in this industry has unfortunately led to many examples where once-through scrubber water is the mode of operation. However, there are several plants notable in this respect which recycle scrubber water from a sump, thus satisfying the scrubber water flowrate demands (based upon mass transfer considerations) while retaining control of water usage. These notable plants are TVA (Muscle Shoals, Alabama), and Plants 003 and 182.

Recycle of scrubber water permits the subsequent treatment of much smaller quantities of waste water with much higher concentrations of polluting constituents. Both of these attributes make waste water treatment more economical, and in some cases, more efficient, from a removal viewpoint.

Dry Dust Collection

A drastic reduction in the aqueous waste load may be made by replacing wet scrubbing systems with baghouses, or alternately, by placing cyclone dust collectors upstream of wet scrubbers. This approach is feasible because baghouses have recently been improved in design to the point where operation and maintenance costs are not excessive, where solids collection efficiences exceed those of wet scrubbers, and where operating temperature ranges have been extended with high-temperature media development. Dry collected solids may be returned to the product stream, provided that a separate collector is installed for each product. This is a change in approach for the typical multi-product phosphate plant, since conventional practice has been to centralize the collection and treatment functions across product lines. With dry separate collection, the product recovered may significantly contribute towards the operating cost of the collectors.

Plants in this industry which are notable in this respect by having at least some dry dust collection include Plants 003, 006, 042, 119, and 182.

Housekeeping and Containment

Containment and disposal requirements may be divided into several categories:

1. minor product spills and leaks
2. major product spills and leaks
3. upsets and disposal failures
4. storm water runoff
5. pond failures
6. vessel and container cleanout

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Minor Spills and Leaks

There are minor spills and leaks in all industrial chemical manufacturing operations. Pumps seals leak, hoses drip, washdowns of equipment, pipes and equipment leak, valves drip, tank leaks occur, solids spill and so on. These are not going to be eliminated. They can be minimized and contained. In some cases the products are valuable; in other cases, personnel safety and prevention of corrosion may become paramount.

Reduction techniques are mainly good housekeeping and attention to sound engineering and maintenance practices. Pump seals or types of pumps are changed. Valves are selected for minimizing drips. Pipe and equipment leaks are minimized by selection of corrosion-resistant materials.

Containment techniques include drip pans under pumps, valves, critical small tanks or equipment, and known leak and drip areas such as loading or unloading stations. Solids can be cleaned up or washed down. All of these minor leaks and spills should then go to a containment system, catch basin, sump pump or other area that collects and isolates all of them from other water systems. They should go from this system to suitable treatment facilities.

Of special importance in the phosphorus-consuming subcategory of the industry is the containment of phossy water from phosphorus transfer and storage operations. While displaced phossy water is nominally shipped back to the phosphorus-producing facility, current practice in phosphorus storage tanks is to maintain a water blanket for safety reasons by makeup water addition and by subsequent overflow over a weir or excess water.

This method of level control is unacceptable since it results in the discharge of phossy water. One way to ensure zero discharge is to install an auxiliary tank to collect phossy water overflows from the phosphorus storage tank; this system can be closed-loop by reusing this phossy water from the auxiliary tank as makeup for the main phosphorus tank. This scheme preserves the positive safety features of the existing level control practice and also safeguards against inadvertent large discharges resulting from leaky or maladjusted water makeup valves.

Major Product Spills and Leaks

These are catastrophic occurrences with major loss of product, tank and pipe ruptures, open valves, explosions, fires, and earthquakes.

No one can predict, plan for or totally avoid these happenings, but they are extremely rare. Probably the most common of these rare occurrences is tank or valve failures. These can be handled by adequate dikes able

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to contain the tank volume. All acid, caustic or toxic material tanks should be diked to provide this protection. Other special precautions may be needed for flammable or explosive substances. Plant 037 is a prime example where product tanks and trsnsfer pumps have been systematically diked for containment or spills.

Upsets and Disposal Failures

In many processes there are short term upsets. These may occur during startup, shutdown or during normal operation. The phosphorus-consuming subcategory and the phosphate subcategory of this industry may be more vulnerable to this type of upset since so many of the processes are batch-type operations with much more direct operator control then the typical large-scale automated continuous processes in the chemical industry.

These upsets represent a small portion of overall production but they nevertheless contribute to waste loads. Hopefully, the upset products may be treated, separated, and largely recycled. In the event that this can not be done, they must be disposed of.

One very special problem in the phosphorus-consuming subcategory is the inadvertent spill of elemental phosphorus into a plant sewer line. Past practice has been to let it remain in the sewer and to ensure a continuous water flow to prevent fire. There has been general reluctance to clean it out since phosphorus burns when exposed to air. With this practice, of course, all water flowing in that sewer from that time on contains phosphorus and ostensibly becomes contaminated.

Provisions can be made for collecting, segregating and bypassing such phosphorus spills. One method is the installation of a trap of sufficient volume just downstream of reaction vessels, with appropriate installations and valving to enable the bypass of that trap after a spill has occurred and the offline removal and cleaning of the trap (with safe disposal of the phosphorus).

Stormwater Runoff

The phosphates segment of this industry is characterized by the handling, storing, conveying, sizing, packaging and shipping of finely-divided solid products. Typically, a phosphates plant has all exterior surface of buildings, equipment and grounds covered with dusts. An area of concern is the pickup of these solids by stormwater either as suspended solids or as dissolved solids. Of course, washing down of these dusts is not acceptable; the dry solids must be collected. Where possible, the solids may be returned to appropriate process streams. Where purity requirements prohibit this return, adequate means for safe disposal of solid wastes must be provided.

Plants 003, 042 and 182 are examples of plants which have positive continual cleanup programs for solids, which minimize stormwater runoff. Most plants (with considerable credit to air pollution abatement practices) have also minimized the quality of airborne dusts.

The very practice of process water segregation discussed previously has led to the direct discharge of stormwater without treatment. Little is known from a quantitative standpoint about the severity of this problem in the phosphates segment of the industry, or to what extent containment and treatment of stormwater is required. In the phosphorus manufacturing segment of the industry, where large quantities of dusts are handled, Plant 159 collects approximately 10 kg/kkg (20 lb/ton) in a settling pond for stormwater and non-contact cooling water.

Pond Failures

Unlined ponds are the most common treatment facility used by the industry. Failures of such ponds occur because they are unlined and because they are improperly constructed for containment in times of heavy rainfall.

Unlined ponds may give good effluent control if dug in impervious clay areas or poor control if in porous, sandy soil. The porous ponds will allow effluent to diffuse into the surrounding earth and water streams. This may or may not be detrimental to the area, but it is certainly poor waste control. Lined ponds are the only answer in these circumstances.

Many ponds used today are large low-diked basins. In times of heavy rainfall, much of the pond content is released into either the surrounding countryside, or, more likely, into the nearest body of water. Again, whether this discharge is harmful or not depends on the effluent and the surrounding area, but it does represent poor effluent control.

Good effluent control may be gained by a number of methods, including:

1. Pond and diking should be designed to take the anticipated rainfall - smaller and deeper ponds should be used where feasible.

2. Control ponds should be constructed so that drainage from the surrounding area does not innundate the pond and overwhelm it.

3. Substitution of smaller volume (and surfaced) treatment tanks, coagulators or clarifiers can reduce rainfall influx and leakage problems.

Vessel and Container Cleanout

One common characteristic of the phosphorus-consuming subcategory of the industry is the planned accumulation of residues in reaction vessels and stills, with infrequent shutdowns to clean and remove these residues. In many cases, the residues are washed down with firehoses and the wastes discharged. This practice is clearly unacceptable. One alternative is the diking of the area (as described previously), with collection and treatment of the aqueous wastes, in conjunction with an effort to minimize the quantities of washwater.

A similar situation exists with regard to the cleaning of returnable containers (drums, tank trucks and tank cars) prior to reuse. Since these are routine operations, procedures and facilities must be made available for minimizing the quantities of waste water and for the collection and treatment of these waste waters.

Monitoring Techniques

Since the chemical process industry is among the leaders in instrumentation practices and application of analytical techniques to process monitoring and control, there is rarely any problem in finding technology applicable to waste water analysis. Acidity and alkalinity are detected by pH meters, often installed in-line for continuous monitoring and control.

Dissolved solids may be estimated by conductivity measurements, suspended solids and turbidity, and specific ions by wet chemistry and colorimetric measurements. Flow meters of numerous varieties are available for measuring flow rates.

The pH meter is the most universal of the in-line monitoring instruments. Spills, washdowns and other contributions become quickly evident. Alarms set off by sudden pH changes alert the operators and often lead to immediate plant shutdowns or switching effluent to emergency ponds for neutralization and disposal. Use of in-line pH meters will be given additional coverage in the control and treatment sections for specific chemicals.

Monitoring and control of harmful materials such as phosphorus and arsenic is often so critical that batch techniques may be used. Each batch can be analyzed before discharging. This approach provides absolute control of all wastes passing through the system. Unless the process is unusually critical, dissolved solids are not monitored continuously. This follows from the fact that most dissolved solids are rather inert. Chemical analyses on grab or composite effluent samples are commonly used to establish total dissolved solids, chlorides, sulfates, and other low ion concentrations.

Summary

The preceding narrative described general treatment practices and in-plant controls. The following discusses specific abatement measures recommended for each subcategory.

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TREATMENT OF WASTE WATERS IN THE PHOSPHORUS SUBCATEGORY

Neutralization of Acidic Waste waters

Virtually every manufacturing process in the phosphate industry results in a raw waste load of significant acidity. In some cases, advantage is taken of the availability of alkaline waste to at least partially neutralize the acid waste streams.

At phosphorus-producing plants, some neutralization of acidic calciner scrubber liquor is achieved by the alkaline slag or by the slightly alkaline slag quench liquor (see Table 7). At TVA, the slag is granulated by quenching with a high-velocity jet of calciner scrubber liquor plus process cooling water; the granulated slag (with its large surface area) effectively neutralizes the acidic liquors. At plants not granulating slag, the slightly-alkaline slag quench liquors are mixed with the highly-acidic scrubber liquors for partial neutralization. This is practiced at Plants 028 and 181.

Except for this one case where granulated slag is available, lime or limestone neutralization of acid waste streams is standard practice in this industry, as observed at Plants 003, 006, 028, 159, 181, and 182. The relative chemical costs reported by Downing, Kunin and Polliot(28), listed in Table 12, show that limestone or lime are far and away more economical than other neutralizing materials. Limestone is the lower cost material (approximately $11/kkg ($10/ton)) but suffers the disadvantages of slower reaction and lower obtainable pH than with lime. Lime costs are approximately $22/kkg ($20/ton).

With the exception of hydrochloric acid from PCl_3 and $POCl_3$ manufacturing facilities, every acid waste in the phosphorus chemicls industry forms insoluble or slightly-soluble calcium salts when treated with lime:

Acid	Calcium Salt	Solubility*, mg/l
H_3PO_4	$Ca(H_2PO_4)_2.H_2O$, MCP	18,000
"	$CaHPO_4.2H_2O$, DCP	200
"	$Ca_3(PO_4)_2$, TCP	25
HF, H_2SiF_6	CaF_2	16
H_2SiO_3	$CaSiO_3$	95
H_2SO_4	$CaSO_4.2H_2O$	2,410
H_2SO_3	$CaSO_3.2H_2O$	43
H_3PO_3	$2\ CaHPO_3.3H_2O$	(Slightly Soluble)

*Between 17°C and 30°C.

It is readily apparent that lime treatment (with excess lime) not only performs neutralization of acidic waste waters from the phosphate

TABLE 12 Relative Chemical Costs for Neutralizing Acid Wastes
Source: Downing, Kunin and Polliot[28]

NEUTRALIZING MATERIAL	Relative Cost per Pound Alkali*	Relative Weight Alkali Required Per Pound Acid			Relative Cost Per Pound Acid		
		H_2SO_4	HCl	H_3PO_4	H_2SO_4	HCl	H_3PO_4
Lump limestone, high Ca	1.16	110	148	165	128	172	191
Lump limestone, dolomitic	1.00	94	127	141	94	127	141
Pulv. limestone, high Ca	1.59	110	148	165	175	235	262
Pulv. limestone, dolomitic	1.37	94	127	141	129	174	193
Hydrated lime, high Ca	3.06	79	107	119	242	327	364
Hydrated lime, dolomitic	2.50	65	87	98	162	217	245
Pebble lime, high Ca	2.07	60	80	90	124	166	186
Pebble lime, dolomitic	1.87	54	73	81	101	136	151
Pulv. quicklime, high Ca	2.18	60	80	90	131	174	196
Pulv. quicklime, dolomitic	1.97	54	73	81	106	144	159
Sodium bicarbonate	20.65	173	233	260	3570	4810	5360
Soda ash	13.08	119	160	179	1560	2090	2340
Caustic soda (50%)	9.96	164	220	246	1630	2190	2450
Ammonia (anhyd.)	5.90	35	47	53	207	277	313
Magnesium oxide	3.90	42	56	63	164	218	246

*Delivered cost including freight.

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manufacturing industry, but also demineralizes most waste waters by precipitating calcium salts. This then produces a solid waste which may be disposed of by landfilling.

The effectiveness of the control specified in the preceding paragraphs is summarized in table 13 for four plants (TVA, 181, 028 and 159). Data for plants 028 and 159 were taken from tables 14 and 15 which include a complete analysis on the intake and effluent waters.

Removal of Anions (Except Chlorides) From Acidic Wastes

Neutralization of acid waste waters with lime also precipitates the calcium salts of all acid wastes in this industry (with the exception of hydrochloric acid from PCl_3 and $POCl_3$ manufacture). This treatment is widespread throughout the phosphate manufacturing industry, and represents a class of treatment technology which has widespread validation and demonstration on plant-scale installations.

Other technologies for removing dissolved solids (except chlorides) are also presented in this section, with a somewhat lesser degree of full-scale validation than lime treatment.

Treatment of Acidic Fluoride Wastes

Acidic fluoride wastes are generated by the phosphorus production segment of the industry and by the defluorination of wetprocess acid in the manufacture of animal-feed grade calcium phosphates. These waste waters containing large quantities of hydrofluoric, fluosilicic and silicic acids are neutralized with lime (which breaks down H_2SiF_6 at high pH) to precipitate calcium fluoride and gelatinous hydrated silica. Lime treatment is standard operating technology at Plants 128, 159, 181 and 182.

Like lime treatment of phosphoric acid, lime treatment of acidic fluoride wastes is enhanced by the decreased solubility of CaF_2 at high pH:

$$CaF_2(s) \longrightarrow Ca + 2F \xrightarrow{2H_2O} Ca + 2OH + 2HF$$

The equilibrium is driven to the far left by the addition of excess lime. The theoretical solubility of CaF_2 may be calcined in much the same manner as outlined for $Ca_3(PO_4)_2$, using the ionization constant of HF and the pure water solubility data for CaF_2.

There has been recent commercial interest in recovering the fluoride values in acidic waste waters. Two commercial processes have been

TABLE 13 Summary of Control & Treatment Techniques at Phosphorus-Producing Plants
(For Process Waters Other Than Phossy Water)

	TSS	Total Acidity (Alkalinity)	TDS	Fluoride	Sulfate	Total Phosphate
Raw Waste Loads (from Sec. V)						
Kg/Kkg	42.5	54.5	-	53.5	111	25
lb /ton	85	109	-	107	222	50
Waste Discharged, Kg/Kkg:						
TVA	0	0	0	0	0	0
Plant 181	0	0	0	0	0	0
Plant 028 (Net)	0.5	1	4	0.1	2	0.2
Plant 159 (Gross)	0.5	(12)	22	0.04	3	0.8
Waste Discharged, lb /ton:						
TVA	0	0	0	0	0	0
Plant 181	0	0	0	0	0	0
Plant 028 (Net)	1	3	9	0.2	4	0.4
Plant 159 (Gross)	1	(24)	45	0.07	7	1.6
Control & Treatment Efficiency, Per Cent:						
TVA	100	100	100	100	100	100
Plant 181	100	100	100	100	100	100
Plant 028	99	-	-	99+	98	99
Plant 159	99	-	-	99+	97	97

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TABLE 14 - Effluent from Plant 028 (Discharge No. 001)

Effluent Flowrate = 103-200 l/kkg (24,700 gal/ton)

Notes: 1. This Discharge is from Cooling Water and Dust Collector Water.
2. There is Zero Discharge of Phossy Water and Calciner Scrubber Water

	Water & Wastewater Analysis				Net Effluent Qty Kg/Kkg		Net Effluent Qty Lb /ton	
Constituent	Units	Intake	Effluent Plant Data	Effluent Ind. Data	Plant Data	Inde-pendent Data	Plant Data	Inde-pendent Data
pH	-	-	7.3-9.5	7.55	-	-	-	-
Turbidity	FTU	26	32	30	-	-	-	-
Conductivity	µmhos/cm	359	408	300	-	-	-	-
TSS	mg/l	15	15	20	-	0.5	0	1
TDS	mg/l	160	202	176	4	2	9	3
$CaCO_3$ Alkalinity	mg/l	116	110	130	(-1)	1	(-1)	3
$CaCO_3$ Acidity	mg/l	-	-	-	-	-	-	-
Chloride	mg/l	<0.1	4.1	8	0.4	0.8	0.9	1.6
Fluoride	mg/l	0.19	1.14	0.87	0.10	0.07	0.20	0.14
Sulfate	mg/l SO_4	6.4	13.8	26	0.8	2.1	1.5	4.1
COD	mg/l	2.0	53.5	25	5.3	2.4	10.6	4.8
Total Hardness	mg/l	116.7	129.7	160	1	4	3	8
Total Phosphate	mg/l PO_4	1.2	2.4	-	0.12	-	0.25	-
Ortho Phosphate	mg/l PO_4	1.2	2.4	2.9	0.12	0.18	0.25	0.35

TABLE 15 Effluent from Plant 159

Notes: 1. There is Zero Discharge of Phossy Water
2. These data are Plant Data, Not Independently Verified

Effluent Flowrate = 36,100 l/kkg (8,640 gal/ton)

Constituent	Units	Water & Wastewater Analysis: Treated Intake	Water & Wastewater Analysis: Effluent	Gross Effluent Quantity: Kg/kkg	Gross Effluent Quantity: lb /ton	Net Effluent Quantity: Kg/kkg	Net Effluent Quantity: lb /ton
pH	-	7.5	8.0-8.5	-	-	-	-
Turbidity	FTU	<1	11	-	-	-	-
Conductivity	$\frac{\mu mhos}{cm}$	966	898	-	-	-	-
TSS	mg/l	11	15	0.54	1.08	0.14	0.29
TDS	mg/l	617	620	22.4	44.8	0.11	0.22
$CaCO_3$ Alkalinity	mg/l	358	323	11.7	23.4	(-1.3)	(-2.6)
$CaCO_3$ Acidity	mg/l	-	-	-	-	-	-
Chloride	mg/l	50	53	1.9	3.8	0.11	0.22
Fluoride	mg/l	0.84	1.01	0.04	0.07	0.0061	0.0122
Sulfate	mg/l SO_4	91.5	90.0	3.2	6.5	(-0.054)	(-0.108)
COD	mg/l	-	6	-	0.2	0.22	0.43
Total Hardness	mg/l	465	468	16.9	33.8	0.11	0.22
Total Phosphate	mg/l PO_4	18.0	22.4	0.8	1.6	0.16	0.32
Ortho Phosphate	mg/l PO_4	15.9	19.3	0.7	1.4	0.12	0.24

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developed to manufacture hydrofluoric acid, and one to manufacture synthetic cryolite for the aluminum industry.

Removal of Suspended Solids

The raw waste streams from the phosphorus-producing segment and from the phosphate subcategory of the industry contain considerable quantities of suspended solids. Moreover, the chemical treatment of acidic wastes described in the previous section produced in many instances, additional suspended solids.

To facilitate settling of suspended solids, large quiet settling ponds and vessels are needed. Settling ponds are the foremost industrial treatment for removing suspended solids. They are in use at Plants 006, 028, 119, 159, 181 and 182. Removal of suspended solids generates a solid waste effluent which must be disposed of by landfilling.

The size and number of settling ponds differ widely depending on the settling functions required. Waste streams with small suspended solids loads and fast settling characteristics can be cleared up in one or two small ponds; others with heavier suspended solids loads and/or slower settling rate may require 5 to 10 large ponds. Most settling ponds are unlined, but the technology exists for lined ponds.

Although not as widely used as settling ponds, tanks and vessels are also employed for removal of suspended solids in the phosphate manufacturing industry. They are in use at TVA (Muscle Shoals, Alabama) and at Plants 003, 006, 028 and 159.

Commercially these units are listed as clarifiers or thickeners depending on whether they are light or heavy duty. They also have internal baffles, compartments, sweeps and other directing and segregating mechanisms to provide more efficient performance. This feature plus the positive containment and control and reduced rainfall influence (smaller area compared to ponds) should lead to increasing use of vessels and tanks in the future, especially where a plant is short of available land for settling ponds.

Filtration equipment, such as plate-and-frame pressure filters, pressure or vacuum leaf filters, rotary vacuum filters, and pressure tubular filters, has been widely used in the chemical and waste treatment field for many years. The batch-type filters find most use in polishing applications, to completely remove small quantities of suspended solids, since the labor-intensive blowdown operation is dependent upon cake volume. These filtrations are common for collection of undesirable solid wastes, such as arsenic sulfide from food-grade phosphoric acid. Continuous rotary vacuum filters find general applicability in dewatering sludges with high concentrations of solids. Sand-bed filtration also finds increasingly-widespread use.

Filtration is in use at Plants 006, 075 and 119 in this industry. In general, filtration is not economically attractive for huge quantities of waste water (except for sand-bed filtration). It is usually preceded by a gravity thickening operation so that it treats the thickened sludge which is only a small volumetric percentage of the total waste water flow.

Centrifugation, in use at Plant 003 and at the TVA installation, is an alternate means for mechnical dewatering of relatively low flow rate sludges, and has made major recent inroads into the domestic waste water treatment field. The continuous solid-bowl centrifuge, as its name implies, provides for continuous removal of the cake, and its design reaches a compromise between solids recovery and cake dryness. The basket solid-bowl centrifuge, on the other hand, discharges cake intermittently, and the dewatering and cake-drying portions of the cycle may be separately controlled. Perforated-bowl centrifuges are really centrifugal filters. The solid-bowl machines offer the significant advantage over filters that blinding of a medium is removed as a problem area.

Dewatering of Lime-Precipitated Phosphates

Although (as previously discussed) lime can be used to effectively precipitate phosphates from solution to reduce the concentration to 0.3 mg/l or less (as PO_4), the lime-precipitated phosphates do not dewater readily, but form a water-trapping gel structure. After 24 hours of settling, clarified effluents still may have 15 to 50 mg/l of suspended solids. This can be significantly improved by increasing the detention time to 7 days, but the suspended solids content may still be 5 mg/l or greater. In the phosphate manufacturing industry, settling ponds with 7 days or longer detention times (equivalent to an overflow rate of 420 lpd/m² (10 gpd/ft²) at a nominal depth of 3 m (10 ft) are used. It has been reported that the settling characteristics are strongly dependent upon the initial concentration of phosphate ion. An initial concentration of 75,000 mg/l resulted in a compacted settled slurry density 3 to 5 times higher than if the initial concentration was 1,500 mg/l.

Where sufficient land area for large settling ponds is not available, average removal efficiencies of 80 to 95 per cent have been obtained with mechanically raked gravity thickeners. A typical thickener design has a 2-hour detention time and an overflow rate of 42,000 lpd/m² (1,000 gpd/ft²).

Synthetic organic, water-soluble, high molecular weight polyelectrolytes have achieved great success in flocculation and clarification and in sludge conditioning prior to centrifugation or filtration. A polymer dosage of 0.05 kg per kkg of dry sludge solids (0.1 lb/ton), or about 1 mg/l of a 2 per cent slurry, may achieve 85 per cent removal of

suspended solids at a detention time of 2 hours, with a 12 per cent solids content in the thickened sludge. If this thickened sludge were then vacuum-filtered, a cake of 30 per cent solids could be obtained with a solids content in the filtrate of 0.5 mg/l of less.

The following may be a typical performance chart for an influent sludge containing 100 liters of water:

	Influent	Thickener Overflow	Thickener Underflow	Filter Cake	Filtrate
Water, Liters	100	84	16	5.1	10.9
Suspended Solids, Kg	2.56	0.38	2.18	2.18	5 x 10-6
Suspended Solids Concentration	2.5%	0.45%	12%	30%	0.5

The dewatered cake, containing 85 per cent of the original solids, may be landfilled. The filtrate, when combined with the thickener overflow, would consist of 95 per cent of the original water quantity and would have a suspended solids concentration of 4,000 mg/l.

A much clearer effluent could be obtained, of course, if all of the influent waste water were directly filtered. Such is the practice at Plant 006, which achieves an average phosphate removal efficiency of 95 per cent.

Mechanical dewatering of lime-precipitated phosphates by centrifugation was attempted, but it proved unsuccessful because the highly thixotropic cake plugged the solids-removal screw.

Because an excess of lime is used in the precipitation of the phosphates, the effluent from the ponds or from mechanical thickening and dewatering would have a high pH, typically 10 to 11. This effluent could be partially carbonated (with CO_2) to reduce the pH to 8.0 to 8.5 prior to discharge, with another filtration step to remove the calcium carbonate precipitate. Alternately, it has been shown that subsequent activated sludge treatment of high-pH waste water at municipal treatment plants lower the pH due to biologically-released CO_2 from the oxidation of organic material.

Treatment Alternatives

There were two treatment alternatives considered for this subcategory. The first alternative is the treatment currently employed by 90 percent of the industry. This includes complete recycle of phossy water, evaporation of some process water, lime treatment, and sedimentation of the remaining water prior to discharge. The second alternative practiced by 10 percent of the industry involved 100 percent recycle of all process water.

TREATMENT OF WASTE WATERS IN THE PHOSPHORUS CONSUMING SUBCATEGORY

Control and Treatment of Phossy Water at Phosphorus Producing Plants

Because of harmful effects of elemental phosphorus in small concentrations in waste water, and because complete removal of the phosphorus from the water is not practical, it is univeral practice at phosphorus-producing plants to reuse the phossy water after treatment (which is required to removed other constituents in the waste water which would otherwise build up to concentration).

Barber(5) discusses several methods tried experimentally to remove elemental phosphorus from phossy water. Among these methods were chlorination, which was tried more than 20 years ago and which was discarded at that time because "accurate chlorinator control was found to be impractical". With the development of chlorine analyzer-controllers for municipal waste water treatment, however, it appears that chlorination deserves another trial. Air-oxidation was attempted, but the reaction was far from complete, leaving 14 to 37 per cent of the original colloidal phosphorus unoxidized. Filtration of the colloidal phosphorus was investigated but found impractical. As a result of these discouraging results, the industry has adopted the route of containment and reuse rather than treatment and discharge.

At the TVA Muscle Shoals plant, a commercial flocculant, at a concentration of 40 mg/l, is employed to settle both the phosphorus and the suspended solids. Using a clarifier, the system removes 92 to 93 per cent of both the phosphorus and the suspended solids as the phosphorus sludge underflow (which is only 2 per cent of the waste water volume). The presence of suspended solids is necessary for efficient removal by this method.

The underflow from the clarifier may be treated as other phosphorus muds or sludges are treated. The sludge may be gravity thickened and/or dewatered by centrifugation or filtration. The sludge, thickened sludge, or sludge cake (with respectively lower moisture contents) may then be heat-dried in an inert atmosphere using the process byproduct carbon monoxide as fuel. Elemental phosphorus (nominally 40 to 65 per cent of the "solids" in the sludge) are recovered. The remaining non-volatile solids contain no elemental phosphorus and can be safely disposed of or recycled to the feed preparation section of the phosphorus manufacturing plant.

The clarifier overflow, containing only 7 or 8 per cent of the original phosphorus and suspended solids, may then be recirculated to the phosphorus condenser sump and to other areas where water contacts phosphorus. However, because the phossy water accumulates dissolved salts (mainly fluorides and phosphates, see Table 7), about 6 per cent of the clarified water must be bled off and discharged. In addition to

suspended solids and dissolved solids, this bleed contains 120 mg/l of elemental phosphorus, equivalent to 0.4 kg/kkg, or 0.08 pound per ton, of product.

At Plant 181, a different approach is taken towards phossy water wastes. Very large lagoons not only reduce the concentration of suspended solids in the phossy water, but also serve to slowly oxidize much of the elemental phosphorus to phosphates. Subsequent lime treatment of the lagoon overflow (after combining with other waste water streams) precipitates not only the phosphates but also the fluorides in the water, thereby reducing the quantity of dissolved salts so that the water may be reused without a bleed. At this plant, the waste streams may be combined since all wastes are recycled without discharge.

A slightly different approach is taken at Plant 128. The phossy water is combined in a closed treatment and recycle system with calciner scrubber liquor. After settling of suspended solids and partial oxidation of phosphorus in a pond, lime treatment is used to precipitate dissolved phosphates and fluorides. Upon subsequent settling, the clarified (but still phossy) water is reused as calciner scrubbing water. Fresh makeup is used for the phosphorus condenser. The key to this scheme, which results in zero discharge of phossy water, is that the quantity of water vaporized in the calciner scrubber (in cooling the calciner tail gases) exceeds the quantity of phossy water in the raw waste load, so that fresh water may be continuously added to the loop without discharging any contaminated water.

Plant 159 achieves zero discharge of phossy water in a rather unique system. The completely segregated raw waste phossy water is sent to a clarifier in a manner similar to the TVA technique described above. The clarifier underflow of phosphorus sludge is treated in conventional ways, with complete return of the material to the process. The overflow from the clarifier is not recycled (as is the TVA practice, which requires a bleed discharge); but is sent to an evaporation pond.

In the approaches used by Plants 028 and 159, some or all of the phossy water is evaporated. This presents no hazard of elemental phosphorus, since it is very rapidly oxidized to phosphate as soon as the protective water is removed.

In summary, this study found three different ways that existing plants are achieving zero discharge of phossy water.

Treatment of Arsenic-Rich Residues

Arsenic-rich solid residues accumulate from the purification of phosphoric acid and of phosphorus pentasulfide. The common disposal method is burial in a controlled area, as practiced at Plants 075, 119, 147 and 192.

The arsenic-rich liquid residue from the PCl_3 distillation is more difficult to dispose of. At Plant 037, this residue is first treated with trichloroethylene, in which PCl_3 is miscible but $AsCl_3$ is not. The trichloroethylene is then water-washed to remove the arsenic-free PCl_3 and the trichloroethylene is reused. The $AsCl_3$-rich residue is then segregated and stored in drums for final disposal in an environmentally safe manner.

Treatment of Phosphoric Acid Wastes

The standard treatment of these wastes is by neutralization and/ or precipitation with lime as discussed for the phosphorus production subcategory. the final product of neutralization in an excess of lime and in a considerable excess of water, is formed:

$$6\ H_3PO_4 + 10\ Ca(OH)_2 \rightarrow 3\ CaO.3\ P_2O_5.Ca(OH)_2 + 18\ H_2O$$

Although this material is very insoluble, the reaction does not proceed to completion in practice unless a Ca/P mole ratio of at least 1.9 is reached. Moreover, the reactivity of the lime in precipitating the dissolved phosphate is strongly dependent upon the lime source and the slaking conditions. It has been found that freshly-slaked pebble quicklime can precipitate in excess of 97 per cent of the phosphate, whereas commercial hydrated lime (calcium hydroxide) or freshly-slaked ground quicklime only succeeded in a 73 to 80 per cent precipitation efficiency under the same conditions.

A large body of literature has been developed in the lime treatment of domestic waste waters for phosphate removal. The study performed by Black & Veatch for EPA(31) summarizes the efforts that have been sufficiently demonstrated to be applied to current municipal waste water treatment projects. It is pointed out that the average concentration in domestic raw waste water is about 10 mg/l (expressed as elemental phosphorus). The domestic sources are about 1.6 kg (3.5 lbs) per capita per year, one-third of which are from human excretions and two-thirds from synthetic detergents.

The existing practice achieves better than 90 per cent removal of the phosphates from domestic waste water, reducing the concentration (expressed as PO_4) from 30 mg/l to as low as 0.3 mg/l. At first glance, this seems to conflict with the fact that tricalcium phosphate (or hydroxylapatite) has a solubility of 25 mg/l (equivalent to 15 mg/l as PO_4). However, in a large excess of lime, the pH is sufficiently high (10 to 11) to reduce the solubility of this salt of a strong base and weak acid. The equilibrium -

$$Ca^{+3}_3(PO_4)_2(s) \xrightarrow{2H_2O} 3Ca^{+2} + PO_4^{-3} \longrightarrow 3Ca^{+2} + 2OH^- + 2HPO_4^{-2}$$

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is driven to the far left (reducing phosphate solubility) by the addition of excess lime. The solubility of tricalcium phosphate may be theoretically calculated as a function of pH (or of Ca:P ratio) using the ionization constants for H_3PO_4, $H_2PO_4^1$, and HPO_4^2 in conjunction with a solubility product for tricalcium phosphate (which may be calculated from solubility data in pure water).

This phenomenon, substantiated by full-scale operating data as reported by Black & Veatch(31), is summarized below:

pH	Phosphate Concentration of Filtered Effluent, mg/l
9.0	5.7
9.5	1.4
10.0	0.6
10.5	0.3
11.0	0.2

The literature is replete with details of technology to achieve high removal efficiencies.(31-42) For example, thickened sludge recirculation to the neutralization tank has been found to seed the precipitation of calcium phosphate, resulting not only in better removal of dissolved phosphates but also in the growth of larger crystals for easier dewatering.

Although lime treatment of phosphates has been the predominant route, ferric chloride and alum have also been extensively used. Ferric salts are most effective in the 4 to 5 pH range and aluminum salts are most effective in the 5 to 6 pH range, as opposed to the 10 to 11 range for lime. The mole ratio of Fe/P or Al/P should be around 2.0, the same as the Ca/P ratio with lime treatment.

The use of lanthanum salts has recently been demonstrated to more effectively precipitate phosphates over a much wider pH range than calcium, ferric, or aluminum. The drawback is cost; the treatment system must recover and reuse the lanthanum.

Another process for phosphate removal is adsorption by activated alumina with subsequent stripping with caustic acid then regeneration of phosphate-free caustic by lime precipitation. Ion exchange has also been investigated.

One interesting process for phosphate removal is borrowed from a commercial process for HCl acidulation of phosphate rock. Phosphoric acid is recovered by solvent extraction, using C_4 and C_5 primary alcohols such as n-butanol and isoamyl alcohol. The chloride-free phosphoric acid is then extracted from the organic phase by water

washing, the solvent is recycled, and the pure phosphoric acid may be concentrated by evaporation of water. This treatment method appears attractive for application to the food-grade calcium phosphate waste streams. The suspended solids may be dissolved by HCl addition, and solvent extraction may be used to regenerate phosphoric acid for return to the process.

Treatment of Acidic Sulfite, Sulfate, and Phosphate Wastes

These acids are components of the waste streams from the phosphorus-consuming subcategory of the industry; and sulfuric acid is also a constituent of the wastes from the phosphorus-production segment. The sulfurous and phosphorus acids may be partially oxidized prior to treatment to sulfuric and phosphoric acids.

The neutralization and precipitation of the slightly soluble calcium salts is exactly comparable to the treatment of acidic phosphate and fluoride wastes. The solubilities of calcium sulfite and of calcium phosphite are repressed by excess lime as in the previously-discussed cases, but the solubility of calcium sulfate (a salt of a strong base and a strong acid) is not affected by pH.

Removal of Chlorides

Ion Exchange and Demineralization

Ion exchange and demineralizations are usually restricted in both practice and costs to total dissolved solids levels of 1000 to 4000 mg/l or less.

An ion exchange may be simply defined as an insoluble solid electrolyte which undergoes exchange reactions with the ions in solution. An exchanger is composed of three components: an inert matrix, a polar group carrying a charge and an exchangeable ion carrying an opposite charge. The inert matrix is usually cross-linked polymeric resin containing the needed polar groups.

There are two types of ion exchangers: cation and anion. Cation exchangers contain a group such as sulfonic or carboxylic acid. These can react with salts to give products such as the following:

$$RSO_3H + NaCl \rightleftharpoons RSO_3Na + HCl$$
$$RCO_2H + NaCl \rightleftharpoons RCO_2Na + HCl$$

The above reactions are reversible and can be regenerated with acid.

Anion exchangers use basic group such as the amino family.

$$RNa_3OH + NaCl \rightleftharpoons RNa_3Cl + NaOH$$

This is also a reversible reaction and can be reqenerated with alkalies. The combination of water treatment with both cation and anion exchanqers removes the dissolved solids and is known as demineralization (or deionization). The quality of demineralized water is excellent. Table 16 gives the level of total dissolved solids that is achieved. Special ion exchanqe systems have been developed for treating hiqh dissolved solids content (more than 1000 mq/liter total dissolved solids), minimizinq regenerant chemicals costs.

Reverse Osmosis

The phenomenon of osmosis has its explanation in thermodynamic equilibrium and free energy concepts. Essentially, when a semipermeable membrane separates a pure liquid and solution of dissolved material in the same liquid there is a net miqration of the pure liquid to the solution, driven by the free energy difference between the two sides of the membrane. Equilibrium is reached only when the liquids on each side of the membrane are of the same composition or sufficient additional pressure is applied on the solution side of the membrane to counterbalance the osmotic drivinq force. Application of additional pressure on the solution side reverses the direction of osmotic flow throuqh the membrane and results in concentration of the solution and miqration of additional pure liquid to the pure liquid side. This is reverse osmosis. It may be looked at as pressure filtration throuqh a molecular pore-sized filter.

The small pore size of the reverse osmosis membrane is both its strength and its weakness. Its strength comes from the molecular separations that it can achieve. Its weakness comes from the criticalness it has to blindinq, pluqqinq, and chemical attack. Acidity, suspended solids, precipitations, coatinqs, dirt, orqanics and other substances can make it inoperative. Membrane life is critical and unknown in many mediums.

TABLE 16 Water Quality Produced by Various Ion Exchange Systems

Exchanger Setup	Residual Silica, mg/l	Residual Electrolytes, mg/l	Specific Resistance ohm-cm @ 25 C
Strong acid cation + weak-base anion	No silica removal	3	500,000
Strong-acid cation + weak-base anion + strong-base anion	0.01-0.1	3	100,000
Strong-acid cation + weak-base anion + strong-acid cation + strong-base anion	0.01-0.1	0.15-1.5	1,000,000
Mixed bed (strong-acid cation + strong-base anion)	0.01-0.1	0.5	1-2,000,000
Mixed bed + first or second setup above	0.05	0.1	3-12,000,000
Similar setup as immediately above + continuous re-circulation	0.01	0.5	18,000,000

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With these restrictions there is little wonder that its industrial applications are few. Fortunately, the phosphorus chemicals industry water purification needs are similar to those of the areas where reverse osmosis has been shown to be applicable -- treatment of brackish water and low (500 mg/l to 20,000 mg/l) dissolved solids removal. Organics are usually absent, suspended solids are low and can be made low rather easily, acidity is easily adjusted, and the dissolved solids are similar to those in brackish water -- sodium chlorides, sulfates and their calcium counterparts.

Evaporation Ponds

Plant 159 utilizes an evaporation pond for disposal of phossy water from phosphorus manufacturing. They may also be reasonably used for other waste water disposal where the waste water quantities are not overwhelming.

The size of an evaporation pond depends upon the climatic differential between evaporation and rainfall:

Evaporation-Rainfall Differential	Pond Area
0.6 m/yr (2 ft/yr)	0.060 ha/cu m/day (560 acres/MGD)
1.2 m/yr (4 ft/yr)	0.030 ha/cu m/day (280 acres/MGD)
1.8 m/yr (6 ft/yr)	0.020 ha/cu m/day (190 acres/MGD)

Evaporation ponds may be either unlined or lined, and should be diked. Use is often made of natural pits, valleys or ponds.

Conventional evaporation ponds are not, of course, among the useful treatments in areas where the rainfall exceeds the evaporation. However, surface aerators (commonly used for aerated lagoons in secondary treatment of organic wastes) can significantly increase the evaporation from a pond by increasing the water/air surface area.

Single-Effect and Multiple-Effect Evaporators

For the treatment of small waste streams, single-effect evaporators are characterized by low equipment costs and by inherent reliability, at the expense of high steam requirements. Conventional multiple-effect evaporators, with 2 to 6 effects, have somewhat higher capital costs, but require much less steam.

Evaporation is a technology, of course, that is aptly demonstrated throughout the chemicals process industry (although not extensively for

the sole purpose of waste treatment), and as such meets the requirements of being currently available.

Refrigerated Condensers for PCl_3 and $POCl_3$

In the standard processes for manufacturing PCl_3 and $POCl_3$, the present industry practice is to use water-cooled condensers to reflux the reaction vapors and to collect the product. Because the vapor pressure of PCl_3 is significantly high (boiling point 76°C (169°F)) at normal condensing temperatures, the raw waste load in the tail-gas water scrubbers contain rather large quantities of the hydrolysis products of PCl_3. The use of refrigerated condensers in place of the water-cooled condensers; or alternately, the use of cold traps downstream of the water-cooled condensers; would drastically reduce the amount of PCl_3 in the tail gas which subsequently becomes acid aqueous wastes:

Temperature, °C	Temperature, °F	PCl_3 Vapor Pressure, mm Hg(27)
-40	-40	3
-20	- 4	13
0	32	38
+20	68	99
+40	104	235

It is apparent that a condensing temperature below -20°C (-4°F) would lower the PCl_3 vapor pressure by an order of magnitude over normal condensing temperatures, and would virtually double the temperature driving force for heat transfer.

Refrigerated condensers are in current use (for $POCl_3$ manufacture using air oxidation) at Plant 037.

Inert-Atmosphere Casting of P_2S_5

The present industry practice is to cast molten P_2S_5 product into shipping containers or into conical forms. When molten P_2S_5 is exposed to the atmosphere, it spontaneously ignites, forming P_2O_5 and SO_2 which are subsequently water-scrubbed.

There are various state-of-the-art techniques available for casting either in an inert atmosphere or in vacuum, to eliminate this source of raw aqueous waste.

Treatment Alternatives

The treatment alternatives considered for the manufacture of phosphoric acid are first no addition treatment (the only discharges are from leaks and spills) and no discharge of any process waste water pollutants to

navigable waters. The latter alternative involves tightened housekeeping and maintenance construction of dikes and dams around pumps, valves, and tanks; construction of sumps and sump pumps; lime treatment of leaks and spills; and landfill of the sludge. This is currently practiced by 10 percent of the industry.

There were two treatment alternatives considered for the manufacture of phosphorus pentoxide: no additional treatment and no process waste water discharge.

Three treatment alternatives were considered for the manufacture of phosphorus pentasulfide. The first involves no additional treatment. The second includes reduction of the volume of waste water discharge by the recycle of scrubber water. The third alternative includes no waste water discharge, lime treatment, settling tanks, recycle of tank overflow back to the process, and landfill of sludge.

Several treatment alternatives were considered for the manufacture of phosphorus trichloride and phosphorus oxychloride. The first alternative is no treatment. The second involves reduction of waste water volume by recycle of scrubber water. The third alternative includes lime treatment, settling tanks, and landfilling of sludge. The fourth alternative involves no discharge of process waste water pollutants to navigable waters.

TREATMENT OF WASTE WATERS IN THE PHOSPHATE SUBCATEGORY

Treatment of Specitic Wastes

Sodium Tripolyphosphate Manufacture

As stated in Section V, three notable plants (006, 042 and 119) achieve no discharge of porcess waste waters. Airborne solids collected in dust collectors from the spray dryer gaseous effluent stream are added to the product. Scrubber water is used to form a slurry with caustic in the initial process neutralization step.

The manufacture of sodium tripolyphosphate is therefore a water consuming process, requiring no waste water treatment.

Calcium Phosphates Manufacture

The amount of airborne solid wastes removed by wet scrubbers can be minimized by preceding wet scrubbers with dry dust collection equipment. Treatment of phosphoric acid, suspended solids and sludges resulting from wet scrubbing has been previously described for the phosphorus production subcategory.

Wet phosphoric acid is frequently used for animal feed grade phosphates. Fluosilicic, hydrofluoric and silicic acid wastes will subsequently result from acid defluorination. Treatment of these parameters has also been discussed previously for the phosphorus production subcategory.

Treatment Alternatives

The only treatment alternative considered for the manufacture of sodium tripolyphosphate is no discharge of process waste water pollutants. This is essentially accomplished by all of this industry through dry dust collection and return of scrubber water to the system.

Two treatment alternatives were considered for the manufacture of feed grade dicalcium phosphate. The first, employed by at least 50 percent of the industry, involves in-process controls for phosphate and lime dusts and phosphoric acid mists. The second alternative inlcudes the above plus lime treatment settling, and recycle of clarified water to the acid scrubbers and landfill of the sludge.

Three treatment alternatives were considered for the manufacture food grade dicalcium phosphate. No treatment is the first alternative. In the second alternative baghouses replace wet scrubbers with product recovery. Approximately 30 percent of the industry is practicing this technology. In the third alternative waste water is treated with lime, filtered, and recycled in the process. The filter cake is landfilled.

Approximately 10 percent of the industry is achieving no discharge of process water pollutants by this technology.

SECTION VIII
COSTS, ENERGY AND NON-WATER QUALITY ASPECTS

INTRODUCTION

The control and treatment technologies applicable to the raw wastes of the phosphate manufacturing industry were discussed in Section VII of this report. In this Section, each of these technologies is reviewed from the following standpoints:

* The cost of applying the technology.
* The energy demands of the technology.
* The impact of the technology upon air quality, solid waste management, noise and radiation.
* The recovery and subsequent use of process materials from raw waste streams, as a result of applying the technology.

A representative hypothetical plant for each chemical produced in the industry is synthesized. Cost-effectiveness data for the plant for the various treatment alternatives (see table 17) appear as table 18. The cost is in terms of both investment cost and equivalent annual cost, and the effectiveness in terms of pollutant quantities is compared to the raw waste load. The discussion of costs and benefits in this Section, however, is formulated to be more generally useful in evaluating the economics for any particular plant within the industry. Costs for a specific plant may be significantly influenced by the following factors which cannot all be incorporated into a single hypothetical plant:

The degree of freedom, which personnel of each plant must retain, to choose among the alternative control and treatment technologies presented in Section VII, to choose from technologies not presented in this report, and to choose any combination or permutation of these technologies.

The cost tradeoffs, which are unique for each plant, between in-process controls and end-of-process treatments; with material recovery being an important parameter.

The real raw waste load for each plant, which may be appreciably different (in either direction) from the standard raw waste loads as presented in Section V. In particular, much greater plant-to-plant variability was observed with respect to production-normalized raw waste water quantities than with respect to production-ion-normalized raw quantities of polluting constituents.

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TABLE 17

TREATMENT ALTERNATIVES

Subcategory	Chemical	Alternative	Description
Phosphorus Producing	P_4 (Fe_2P)	A	Existing control complete recycle of phossy water. Evaporation of some other process water. Lime treatment and sedimentation of remaining process water prior to discharge.
		B	Piping, pumping, and controls for 100% recycle of process wastewaters.
Phosphorus Consuming	H_3PO_4	A	No treatment. (Only wastewaters orginate from leaks, spills, etc.)
		B	Tighten housekeeping and maintenance. Dike and dam around pumps, valves,, tanks, etc. Provide sumps and sump pumps. Treat with lime and landfill the sludge.
	P_2O_5	A	No treatment.
		B	Lime treatment, settling tank, recycle of tank overflow back to process, and landfill sludge.
	P_2S_5	A	No treatment.
		B	Recycle scrubber water.
		C	Lime treatment, settling tank, recycle tank overflow back to process, landfill sludge + B.
	PCl_3	A	No treatment.
		B	Recycle scrubber water.
		C	Lime treatment, settling tank and landfill sludge + B.
		D	Evaporation + B + C.
	$POCl_3$	A	No treatment.
		B	Recycle scrubber water.
		C	Lime treatment, settling tank, and landfill sludge + B.
		D	Evaporation + B + C.
Phosphate Producing	$Na_5P_3O_{10}$	A	Dry dust collection already in existance at exemplary plant. May be economically justified on the basis of product recovery.
	$CaHPO_4$	A	In-process controls for phosphate and lime dusts and for phosphoric acid mists, including dry dust collection and scrubber water recycle to process.
		B	Lime treatment, settling pond, recycle of clarified water to acid scrubbers, and landfill sludge. + A.
	$CaHPO_4$ Feed grade	A	Replace wet scrubbers with baghouses.
		B	Lime treatment, filtration of slurry, recycle of filtrate, and landfill of filter cake + A.

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TABLE 18

TREATMENT ALTERNATIVES
COST - EFFLUENT QUALITY COMPARISON

Chemical	Treatment Alternative	% Industry Using Alternative	Investment $1,000	Annual Operating Costs $1,000	Cost Per Units $/Kkg	Wastewater l/Kkg	TSS Kg/Kkg	TDS Kg/Kkg	Acidity Kg/Kkg	F Kg/Kkg	SO_4 Kg/Kkg	PO_4 Kg/KKg	H_3PO_4 & H_3PO_3 Kg/Kkg	H_3PO_4 Kg/Kkg	H_2SO_3 Kg/Kkg	HCl Kg/kkg	HF, H_2SiF_6 H_2SiO_3 Kg/Kkg	pH
P	Subcategory																	
P_4	Raw Waste	-	-	-	-	426,000	42	-	54	54	111	25						
	A	90	-	-	-	104,000	0.5	4	1.5	0.1	2	0.2						
	B	10	500	228.2	5.07	0	0	0	0	0	0	0						
P	Consuming Subcategory																	
H_3PO_4	Raw Waste (A)	90	-	-	-	8												
	B	10	95	42.9	0.67	0												
P_2O_5	Raw Waste (A)	100	-	-	-	500							0.2					
	B	0	20	9.1	1.54	0							0					
P_2S_5	Raw Waste (A)	100	-	-	-	30,000							0.5	1				
	B	0	12.5	5.6	0.44	3,000							0.5	1				
	C	0	49.5	22.8	1.87	0							0	0				
PCl_3	Raw Waste (A)	100	-	-	-	5,000	-	-					2.5			3		2
	B	0	4.2	1.8	.17	500	-	-					2.5			3		1.5
	C	0	16.5	8.8	.77	420	0.7	5					0			0		6-10.5
	D	0	20.5	18.3	1.54	0	0	0					0			0		-
$POCl_3$	Raw Waste (A)	100	-	-	-	2,500	-	-					0.5			2		2
	B	0	2.2	1.0	.16	250	-	-					0.5			2		1.5
	C	0	14.2	6.9	.94	210	0.2	3.5					0			0		6-1-.5
	D	0	15.9	10.1	1.38	0	0	0					0			0		-
P	Subcategory																	
$Na_5P_3O_{10}$	Raw Waste	-	-	-	-	0												
	A	100	*	*	*	0												
$CaHPO_4$	Raw Waste	-	-	-	-	6,700	22					4					12	
(Feed Grade)	A	50	*	*	*	6,300	22										12	
	B	50	186	91.6	1.54	0	0										0	
$CaHPO_4$	Raw Waste	60	-	-	-	4,200	100								30			
(Food Grade)	A	30	*	*	*	2,100	50								15			
	B	10	33	97.2	1.65	0	0								0			

* Use of dry dust collection and product recovery will cover cost of this alternative, hence, no costs were listed.

There is a wide variation in the existing application of of effluent control technology. (i.e.some plants have more equipment to install than others in order to meet the effluent limitations guidelines).
In addition physical characteristics of each particular plant will affect treatment costs such as:

* Plant age, size, and degree of automation.

* Plant layout (i.e., can in-process controls be physically installed between existing units?).

* Plant distances and topography (i.e., what are the installation and operating costs of recycle technologies?).

* Climatic factors (temperature and evaporation/ rainfall).

* Esthetic factors (i.e., is a settling pond locally acceptable?).

* Land availability (primarily a factor in applying settling pond and evaporation pond technologies).

The degree to which a plant is integrated with other production departments would significantly affect the cost of applying control and treatment technologies. Can waste materials from one department be used in an adjoining department (i.e., mutual neutralization of acid and alkaline wastes)? Can common treatment facilities be built (tradeoff between economies of scale vs. reversing the principle of segregation of wastes)? Are the waste water sewers from adjoining departments readily separable?
The feasibility and attractiveness of joint municipal/ industrial waste water treatment, which is a highly local evaluation to be made. Increasingly more examples of such dual treatment are being reported.

The local solid waste management situation. The sludges from applying waste water treatment technologies may be landfilled at highly different costs, depending upon the local availability of disposal sites and the distances involved.

In appreciation of all of the above factors, the discussion of costs in this Section is formulated to be generally useful in evaluating the economics for any particular plant within the industry.

Definition of Representative Plants

The sizes of the representative plants were chosen so that their capacities were approximately the averages of the data presented in Table 2. Although in many cases (especially in the phosphorus-consuming segment of the industry) more than one product is made at a given location, each product was addressed separately in this supplement. Cost savings due to combined treatment facilities are a distinct probability; the effect in practice would be to achieve the benefits at costs lower than those presented in this analysis.

The particular assumptions in choosing representative plants were:

1. Phosphorus Manufacture--The representative plant has already no discharge of phossy water (as much of the industry has). It has, in addition, achieved a level of effluent reduction commeasurate with that of plant 028 (see Tables 13 and 14, but still discharges 25,000 gallons of treated process water per ton into a receiving stream. Technology "A" of Table 17, therefore, represents effluent reduction, with respect to the raw waste load, already achieved by the representative plant, with no additional costs required. The effluent from technology "A" is suitable for process reuse, and technology "B" is the implementation of this recycle. For the representative plant, it was assumed that the return water system traversed 1,000 yards back to the head end of the plant and had a difference in elevation of 60 feet to make up. It was also assumed that the representative plant had no severe freezing problems.

2. Phosphoric Acid Manufacture--The representative plant had no process water discharge (including phossy water), but had not yet performed a systematic and thorough program for minimizing, collecting, and treating minor phosphoric acid leaks and spills.

3. Manufacture of P_2O_5, P_2S_5, PCl_3, and $POCl_3$--The representative plants for these chemicals had not yet instituted any control or treatment of acid waste waters, but have already achieved zero discharge of phossy water. As a conservative approach for PCl_3 and $POCl_3$ manufacture, it was assumed that solar evaporation for technology "C" in Table 17 was not feasible for climatic reasons so that mechanical evaporators were necessary. It was also assumed that refrigerated condensers proved less economical than larger evaporators.

The representative plants for P_2O_5, P_2S_5, PCl_3, and $POCl_3$ are assumed not to have sufficient land for settling ponds, so that mechanically-raked clarifiers are used.

4. Sodium Tripolyphosphate Manufacture--The representative plant has either of two situations: (a) Dry dust collection with return of solids to the process, plus return of wet scrubber liquors to the process, has already been installed resulting in zero discharge of process waste waters. (b) The above controls have not been installed, but can be economically justified on the basis of product recovery.

For either of these two situations (which cover much of the industry), no additional costs (attributable to effluent reduction benefits) are required.

5. Feed-Grade Dicalcium Phosphate Manufacture--For control of phosphate and lime dusts and phosphoric acid mists, the representative plant has no additional required costs (attributable to effluent reduction benefits), for the same reasons as listed above for sodium tripolyphosphate manufacture.

However, it is assumed that the representative plant uses wet-process phosphoric acid and that it performs defluorination of all acid used (in practice, a good fraction of received acid may already be defluorinated). It is further assumed that the representative plants have sufficient land area for on-site settling ponds.

6. Food-Grade Calcium Phosphate Manufacture--The representative plant is assumed to have wet scrubbers for dust-laden vent streams. Technology "A" of Table 17 is the replacement of wet scrubbers with baghouses, but that the cost is justified by product recovery. It is assumed that at this representative plant the elimination of wet scrubbers reduces the waste load by 50 percent.

Current Selling Prices

Table 3 shows the current list prices of the chemicals within this industry. These data are useful as a yardstick for measuring the economic impact of achieving pollution control.

Capital Cost Basis

For these analyses, the capital investment costs have been adjusted to 1971 dollars using the Chemical Engineering Plant Cost Index (1957-59 = 100; 1971 = 132.2). The capital recovery segment of the annual costs are based upon a 5-year amortization schedule, consistent with IRS regulations concerning pollution-abatement equipment and facilities; and upon an 8 percent interest rate. The resulting annual capital recovery factor (principal and interest) is 0.25046.

"Taxes and Insurance" annual cost is estimated at 5 percent of the investment cost. "Operating and Maintenance" annual cost includes labor, supervision, lab support, etc., and is estimated at 15 percent of

the investment cost, exclusive of chemicals, energy and power costs (which are calculated directly for each appropriate case). Chemical costs are included in "Operating and Maintenance", but power is listed separately. The cost of lime for neutralization has been assumed at $20 per ton, and the cost of steam for evaporation has been assumed as $0.70 per thousand pounds (or $0.70 per million BTU).

In-Process Controls

The cost of these controls are perhaps the most difficult to generalize, since they are almost wholly dependent upon the existing equipment configuration in any particular plant.

Segregation of Waste Streams

First, a plant must be surveyed to pinpoint the sources of both process water and non-contact cooling water. At one plant, there were a great many points where process water entered a common sewer, but there were relatively few cooling water sources. It was much more economical to divert the cooling water to a new and separate collection system than to adopt the reverse strategy. The project costs for such a retrofit would be highly labor-intensive, especially since the construction must proceed without unduly disrupting production schedules. Other than capital recovery and associated annual costs, the annual costs would consist of a small maintenance cost and no costs for operating labor, materials or power.

There would be no effect of this project on energy demands, since plant sewers are normally gravity-flow. There would be no adverse non-water quality impacts of this project.

Recycle of Scrubber Water

The capital costs would be to provide a surge tank, a recycle pump, and associated piping. The surge tank need not be large; a 15-minute residence time should suffice. The power costs and energy use of the pump would not greatly exceed the corresponding values presently utilized to provide fresh scrubber water at comparable flow rates; in any event they are small since scrubber flow rates are small.

Dry Dust Collection

Based upon data furnished by the personnel of Plant 007, the capital cost of high-temperature baghouses for this 91 kkg/day (100 tons/day) plant was $350,000. The annual operating and maintenance costs, other than capital recovery, taxes and insurance, is estimated at 6 per cent of the capital cost. A credit to the annual cost is the value of recovered material; the quantity might be estimated as 2 to 5 per cent of the production rate, since baghouses recover virtually all dusts.

The power requirements for the fans and shakers are small, and are usually comparable to the pump power requirements for the liquid scrubbing systems they replace. Since the recovered dusts are almost always utilized in the process, there is no adverse impact upon solid waste management.

Refrigerated Condensers

The condensers are standard items, and in practice the existing condensers may be used. The refrigeration supply is standard equipment, and rather expensive in terms of capital costs. An added cost would be the insulation of existing coolant line and of the condenser. The power requirement for the refrigeration compressor could be moderately high. There would be not impact upon non-water quality aspects.

Inert-Atmosphere Casting for P_2S_5

This is a relatively expensive control technique, requiring major revisions not only of the casting equipment but also of the basic casting procedures. There would be some small power requirement either for inert-gas blowers or for vacuum pumps. The annual cost of the inert gas (assuming it is not recycled) must be estimated.

Housekeeping and Containment

Like the previously-discussed project of water segregation, housekeeping and containment capital costs are labor-intensive and depend to a very large extent upon the existing plant configuration. A point of reference might be taken from the experience of one 360 kkg/day (400 tons/day) plant which expended $160,000 for isolation and containment (trenches, sewers, pipelines, sumps, catch basins, tanks, pumps, dikes and curbs). The need to attend to many small sources of leaks and spills reduces the economies of scale. The power requirements are minimal, limited to small sump pumps. No adverse non-water quality impacts arise from this control technique.

TREATMENT OF SPECIFIC WASTE CONSTITUENTS

Neutralization of Acidic Waste waters and Precipitation of Calcium Salts

A general cost factor for neutralization is 1.3 to 5.3 cents per cu m (5 to 20 cents/1,000 gallons). However, the cost for lime is directly dependent not upon the waste water quantity but upon the total acidity. The data of Table 8, with a lime cost of $22/kkg ($20/ton), can be used to calculate this cost.

Neutralization tanks are usually small, with residence time varying from 30 seconds to 30 minutes. The installed cost of these tanks may be approximated by:

$$\text{Capital Cost} = \$15{,}000 \left(\frac{\text{GPD}}{10{,}000}\right)^{0.2}$$

(Note: l/day = 3.785 x GPD)

The power requirements for mixing are rather nominal. Assuming subsequent sedimentation or other dewatering operations, the neutralization step alone does not have any adverse non-water quality impacts.

Treatment of Arsenic-Rich Residues

The cost of this solvent is rather nominal because the quantities of waste involved are only a very small fraction of the production volume, and because the solvent (trichloroethylene) is reused; despite the high unit costs which is more than 10 cents/cu m (40 cents/1,000 gal). There is virtually no power requirement. There is,however, a very substantial impact upon solid waste management, since the residues are extremely objectionable and must be disposed of in special ways. The quantity involved is 0.05 kg of $AsCl_3$ per kkg of product PCl_3 (0.1 lb/ton).

Control and Treatment of Phossy Water

Control and treatment of phossy water is a universal practice at phosphorus-producing plants. Although several different methods were observed, every plant prevents the discharge of virtually all elemental phosphorus. This technology is therefore so universally applied that costs need not be estimated -the price has already been paid. Similarly, a discussion of energy and of non-water quality aspects would be academic.

Removal of Suspended Solids

Settling Ponds

Using a detention time of 7 days and a depth of 3 m (10 ft), the calculated overflow rate is 0.42 cu m/day/m2 (10 gpd/ft2). This is equivalent to 4,200 cu m/day/hectare (435,600 gpd/acre).

The capital costs for small unlined ponds, with areas from 0.4 to 2 hectares (1 to 5 acres) can be estimated as:

$$\text{Capital Cost} = \$50{,}000 \times \text{Acres} - \$8{,}000 \times (\text{Acres})^2$$

(Note: Hectares = 0.405 x Acres)

Because diking is a large portion of pond costs, and because the dike length increases much more slowly than pond area, larger ponds are considerably cheaper per unit area. For large unlined ponds of 40 to 1,000 hectares (100 to 2,400 acres), the capital cost is $2,500 to $12,500 per hectare ($1,000 to $5,000 per acre).

For lined ponds, the additional installed capital cost for a 30-mil PVC liner is $21,500 per hectare ($8,700 per acre). By using the above overflow rate and the above pond costs per unit area, a pond cost based on waste water flow may be calculated.

Settling ponds utilize no energy. The solids do, however, collect on the bottom and must either be periodically removed (creating a solid waste disposal problem); or the filled pond may be abandoned and replaced with a new one (creating a land use problem).

Mechanically-Raked Clarifiers and Thickeners

A general cost for gravity thickening is 0 to 2.6 cents per cubic meter (0 to 5 cents per 1,000 gallons).

The installed cost of mechanically-raked clarifiers and thickeners with capacities of 38 to 38,000 cu m/day (0.01 to 10 MGD) can be estimated as

$$\text{Capital Cost} = \$95{,}000\ (\text{MGD})^{0.4}$$

(Note: Cu m/day = 3,785 x MGD)

Where polymeric flocculants are used, the additional cost amounts to $4 per kg of flocculant ($1.80/lb). The dosage rate is nominally 0.05 kg/kkg of dry sludge solids (0.1 lb/ton).

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The power requirements are nominal, since the rake has a very long period of revolution. Additional nominal power requirements arise from sludge pumping and clarifier overflow pumping.

This treatment has (by definition) a solid waste impact, since its function is the removal of suspended solids. The sludge from thickeners may be 85 to 92 per cent moisture. If the quantities are small, this sludge may be directly transported to landfills. Alternately, it may be dewatered on sand drying beds or mechanically (filters or centrifuges) to 60-70 per cent moisture before landfilling. The quantity to be landfilled is therefore a very strong function of the degree of dewatering after thickening.

Vacuum Filtration and Centrifugation

The costs of these two mechanical dewatering techniques are competitive. A general cost for either is 0 to 2.6 cents per cubic meter (0 to 5 cents per 1,000 gallons).

The installed capital costs for either vacuum filters or centrifuges are as follows:

Capacity, MGD	cu m/Day	Installed Cost
0.01	38	$25,000
0.1	378	25,000
1	3785	200,000
10	37850	750,000

Polymeric flocculants are often used to condition the sludge prior to dewatering. These costs were discussed in the previous paragraph.

The power requirements for vacuum filtration are moderate; they include the sludge pump, the flocculant pump, the rotating conditioning tank, the vacuum filter drum drive, the sludge agitator below the filter drum, the vacuum pump, the filtrate pump and the cake conveyor belt. Centrifuges have much larger power requirements, since the sludge must be accelerated to hundreds or several thousands of G's. At high speeds, the windage losses (air friction) of centrifuges are considerable. Large centrifuges may require 40 to 75 Kw (50 to 100 HP) of power. Auxiliary power is also required for sludge pumping, flocculant pumping, centrate pumping, the cake scraper, and the cake conveyor belt.

Vacuum filters and centrifuges have a beneficial impact upon solid waste management. Rather than landfilling 12 per cent sludge, these devices drastically reduce the solid waste quantity by producing a 30 to 40 per cent cake.

Centrifuges have a moderately adverse impact with regard to noise pollution, since they run with a characteristic high speed whine that is annoying to the human ear. Vacuum filtration is also a noise contributor since vacuum pumps are noisy machines.

Landfilling of Solid Wastes

The disposal costs for solid wastes are highly dependent upon the hauling distance. The landfill operations alone may cost $6 or more per kkg (or per ton) for small operations and $2 to 4 per kkg (or per ton) for larger operations.

Several pertinent papers have recently been published on the subject of solid waste management in the chemical industry.(63,64)

Solid waste hauling and the material handling operations at landfills are energy-consuming operations. Landfilling of containerized soluble solids in plastic drums or sealed envelopes is practicable but expensive. Blow-molded plastic drums, made from scrap plastic (which is one of the present major problems in solid waste disposal) could be produced for $11-22/kkg ($1020/ton) capacity at 227 kg (500 pounds) solids/drum and a rough estimate of $2.50-$5.00 cost/drum. A more economical method, particularly for large volumes, would be sealed plastic envelopes, 750 microns (30 mils) thick.

At $1.10/kg (50¢/lb) of film, low density polyethylene costs about 10¢ per 0.0929 square meter (1 square foot). Using the film as trench liner in a 1.8 meters (6-foot) deep trench, 1.8 meters (6-foot) wide, the perimeter (allowing for overlap) would be approximately 7.5 meters (25 feet). At a density of 1.6 grams/cc (100 pounds/cubic foot) for the solid, costs of plastic sheet per metric ton would be $2.00 ($1.75/ton). With sealing, the plastic envelope cost would be approximately $2.20/kkg ($2/ton). With landfill costs of $2.20/kkg ($2/ton) additional, the total landfill disposal costs would be about $4.40/kkg ($4/ton).

The above figures for solubles disposal using plastic containers, bags or envelopes are only rough estimates. Also, the technology would not be suitable for harmful solids or in situations where leaching contamination is critical.

Removal of Chlorides

Demineralization and Reverse Osmosis

These treatments are costly, over 10 cents per cubic meter (40 cents per 1,000 gallons).

The installed capital costs can be calculated from:

a. Demineralization, Cap. Cost = $280,000 (MGD) 0.75

b. Reverse Osmosis, Cap. Cost = $480,000 (MGD) 0.75

Hence, the capital costs for reverse osmosis are nearly double those for demineralization.

The operating costs (not including capital recovery costs) are:

a. Demineralization, 20 cents/1,000 gal @ 1,000 mg/l TDS
40 cents/1,000 gal @ 2,000 mg/l TDS

b. Reverse Osmosis, 38 cents/1,000 gal @ 0.01 MGD
20 cents/1,000 gal @ 0.1 MGD
14 cents/1,000 gal @ 1 MGD

Neither demineralization nor reverse osmosis require a great deal of power, and neither has significant non-water quality impact.

Solar Evaporation Ponds

The installed costs of solar evaporation ponds (on the basis of pond area) are essentially the same as the costs for settling ponds presented earlier. The pond area depends in this case upon the climatic differential between evaporation and rainfall:

Evaporation-Rainfall Differential	Pond Area
0.6 m/yr (2 ft/yr)	0.060 ha/cu m/day (560 acres/MGD)
1.2 m/yr (4 ft/yr)	0.030 ha/cu m/day (280 acres/MGD)
1.8 m/yr (6 ft/yr)	0.020 ha/cu m/day (190 acres/MGD)

The power requirements and non-water quality aspects of solar evaporation ponds are the same as for settling ponds. However, since the residue in this case is soluble, extra disposal precautions must be taken to prevent leaching into groundwaters.

Single-Effect and Multiple-Effect Evaporators

The installed capital and operating costs for single-effect evaporators and for a 6-effect evaporator (all stainless-steel construction) are as follows:

Capacity, GPD	Installed Capital Costs, 1 Effect	Installed Capital Costs, 6 Effects	O & M Costs, $/1,000 gal, 1 Effect	O & M Costs, $/1,000 gal, 6 Effects
10,000	8,000		5.64	
50,000	28,000		5.51	
100,000	45,000	177,000	5.45	1.30
250,000	80,000	373,000	5.39	1.22

500,000	146,000	665,000	5.36	1.18
1,000,000	267,000	1,225,000	5.33	1.14

(Note: Liters = 3.785 x Gallons)

The energy requirements for single-effect evaporators are 555 kg-cal per kilogram of water evaporated (1,000 Btu/lb); while the 6-effect evaporator requires 100 kg-cal per kilogram of water evaporated (180 Btu/lb). The non-water quality aspects are the same as for solar evaporation ponds.

NON-WATER QUALITY IMPACT

Air Pollution

The proposed guidelines are not expected to increase air emissions. In fact, the cited technologies should decrease air emissions in some cases where dry air pollution equipment is suggested to precede wet scrubbers. Volatilization of hazardous substances, such as fluorine, from ponds is not expected to present a problem since addition of lime will precipitate most fluorides.

Solid Waste

Solid waste disposal will be the chief non-water quality area impacted by the proposed guidelines. Neutralization of acidic waste streams with lime or limestone will increase the amounts of sludge, especially when soluble phosphates and sulfates are precipitated. Installation of dry air pollution control equipment will reduce the water content of wasted solids. In addition return of collected solids to the process may be feasible. As stated in section VII, arsenic rich solid residues accumulate from the purification of phosphoric acid and of phosphorus pentasulfide. Burial in a controlled area is the standard disposal method. Special disposal methods as mentioned previously in this section may be necessary to prevent leachate from reaching surface or ground waters. Solid waste quantities and constituents are listed in Tables 9 and 10.

Energy Requirements

The energy requirements for the proposed treatment technologies are listed in table 19. For the best practicable control technology currently available the added energy requirements are insignificant when compared to the process energy requirements. Except for the production of phosphorus, energy does not significantly enter into the product cost. For best available technology economically available, the additional energy requirements for PCl_3 and $POCl_3$ are substantial. This is due to the assumption that solar evaporation ponds

TABLE 19

ENERGY REQUIREMENTS
FOR RECOMMENDED GUIDELINES

Chemical	Process Energy Requirement KWH/Kkg	Treatment Energy Requirement KWH/Kkg	Percentage Energy Increase
P_4	15,400	7.06	0.05
H_3PO_4	48	0.000025	0.01
P_2O_5	94	0.0126	0.01
P_2S_5	9	0.75	8.3
PCl_3 (BPCTCA)	27	0.13	0.48
PCl_3 (BATEA)	27	293	1000
$POCl_3$ (BPCTCA)	28	0.063	0.22
$POCl_3$ (BATEA)	28	146	520
$Na_5P_3O_{10}$	43	0	0
Calcium Phosphates animal feed grade	-	0.16	-
Calcium Phosphates food grade	-	0.053	-

BPCTCA - best practicable control technology currently available

BATEA - best available technology economically achievable

may not be possible in a given locale and evaporators may be necessary.

Ground Water

Since settling pond evaporation ponds are extensively used for waste water treatment in the phosphate industry, it is highly recommended that all such ponds be sealed or lined so as to prevent any leakage of contaminated process waters to ground waters.

Noise

No overall adverse affect on the level of noise is expected, although individual equipment may have excessive noise levels (e.g. pumps and centrifuges).

SECTION IX

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE, EFFLUENT GUIDELINES AND LIMITATIONS

INTRODUCTION

The effluent limitations which must be achieved by July 1, 1977 are based on the degree of effluent reduction attainable through the application of the best practicable control technology currently available. For the phosphate industry, this level of technology is based on the best existing performance by notable plants of various sizes, ages and chemical processes within each of the industry's categories. In some cases where no truly notable plants were surveyed, this level of technology is based upon state-of-the-art unit operations commonly employed in the chemical industry.

Best practicable control technology currently available emphasizes treatment facilities at the end of a manufacturing process but also includes the control technology within the process itself. Examples of in-process control techniques which are used within the industry are:

* manufacturing process controls
* recycle and alternative uses of water
* recovery and/or reuse of waste water constituents
* dry collection of airborne solids instead of (or prior to) wet scrubbing.

Consideration was also given to:

a. The total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application;

b. The size and age of equipment and facilities involved;

c. The process employed;

d. The engineering aspects of the application of various types of control techniques;

e. Process changes;

f. Non-water quality environmental impact (including energy requirements).

PROCESS WASTE WATER GUIDELINES

Process water is defined as any water coming into contact with raw materials, intermediates, products, by-products, or gas or liquid that has accumulated such constituents. All values of guidelines and limitations for total dissolved solids (TDS), total suspended solids (TSS), metals and harmful pollutants and and other parameters are expressed as consecutive 30 day averages in units of pounds of parameter per ton and kilograms of parameter per metric ton of product produced except where expressed as a concentration.

Based upon the information contained in Sections III through VIII of this report, the following determinations were made on the degree of effluent reduction attainable with the application of the best practicable control technology currently available in the phosphate manufacturing industry.

The Phosphorus Production Subcategory

Phossy Water

Because of the extremely harmful nature of elemental phosphorus, it is standard practice within the industry to maintain tight control over the discharge of phossy water, as discussed in Section VII.

TVA at Muscle Shoals, Alabama segregates phossy water from all other process and cooling waters, treats the phossy water, and then recycles the treated water back to the process. The clarifier underflow is recycled back to the process, but because of the buildup of dissolved solids, about 6 per cent of this clarified water is bled off.

It is apparent from the discussion in section VII that existing practicable technology can eliminate the requirements for any discharge at this TVA plant. Lime treatment of the blowdown followed by sedimentation of the precipitated phosphates and fluorides would remove the materials necessitating a blowdown, so that this treated blowdown could be recombined with the remainder of the clarified phossy water for return to the process.

There are three examples of plants which have achieved zero discharge of phossy water: Plants 159, 028, and 181.

Hence, three plants have recognized the undesirability of elemental phosphorus in any discharge and have also recognized that no practicable treatment system can remove a sufficient amount of elemental phosphorus to permit effluent discharge of phossy water wastes. They have all solved this dilema by evaporating sufficient phossy water rather than by discharge. One plant uses an evaporation pond, while two others exploit other process heat loads for in-process water evaporation.

In view of this clear-cut demonstration within the industry, it is recommended that the best practicable control technology currently available for phossy water wastes be no discharge of pollutants to navigable waters.

Process Waters Other Than Phossy Water

The standard techniques for treating the waste waters from calciner scrubbers and from slag quenching are lime treatment and settling ponds, which perform the following functions:

* Neutralization of acid waste waters
* Sedimentation of much of the original suspended solids in the waste waters (silica, iron oxide, and others)
* Precipitation and sedimentation of much of the phosphates, fluorides and sulfates which were dissolved in the original waste waters.
* Dissipation of the process heat to the atmosphere during the extended residence in the settling ponds.
* Reduction in the waste water quantity as a result of net evaporation during the extended residence in the settling ponds.
* Where phossy water is combined with these other process waters, some oxidation of the elemental phosphorus to phosphates is accomplished.

At Plant 181, the lime-treated water from all sources is clarified in settling ponds, and the clarified water is held in reuse water supply ponds. There is total recycle of all water at this plant, with zero discharge. Because phosphates and fluorides are removed by lime treatment and sedimentation, there is no requirement to bleed off water for the control of dissolved solids.

Under conditions of very abnormally-high rainfall which would exceed the capacity of the pond system, the only overflow would be from the final reuse water supply ponds, thereby minimizing the quantities of pollutants even occasionally discharged. The recirculating water system runs at a water deficit, due to evaporation in the process and to net evaporation in the pond system. Hence, fresh makeup water is supplied, and can be controlled to compensate for temporary swings in the pond evaporation/rainfall balance.

The TVA plant at Muscle Shoals, Alabama granulates the slag by quenching with a high-velocity jet of water which is recirculated from a sump in the slag pit. In this TVA operation, the cooling water and the scrubber liquors are used for makeup in slag quenching. The granulated slag effectively neutralizes these waters and also acts to filter out the

scrubbed solids, which become part of the slag pile to be sold. Nearly all of the soluble phosphate and 95 per cent of the fluoride is removed by the slag, and the fluoride concentration is reduced to 30 mg/l. Hence, TVA utilizes slag treatment instead of lime treatment, made possible because the slag is finely-divided. Sufficient waste water treatment is obtained by TVA to enable the plant to completely reuse this water without any discharge.

Two other phosphorus plants which utilize lime treatment and sedimentation for process water treatment are Plants 028 and 159. Tables 14 and 15 list (respectively) the effluent concentrations and quantities discharged from these plants, neither of which recycle treated waste water. There are three significant differences between these two plants:

* Plant 028 discharges into the same waterway as the plant intake so that its discharge responsibility is the net increase in constituent quantities. Plant 159 intakes ground water and discharges into surface water so that its responsibility is the gross amount of constituent quantities.

* It is apparent from the "Intake" columns of Tables 14 and 15 that the intake of Plant 159 contains much more dissolved solids (and specifically F, PO_4 and SO_4) than the intake of Plant 028.

* The waste water quantity per cent of production for Plant 028 is three times that of Plant 159.

The above three differences are interrelated and affect the quantities of fluoride, phosphate and sulfate discharged by Plant 159 because the effluent concentrations are of the same magnitude of the solubilities of the corresponding calcium salts. Hence, the effluent quantities are significantly influenced by factors other than the treatment of the process waters.

The effectiveness of control and treatment techniques used by the four phosphorus plants cited are summarized in Table 13. Plants 028 and 159 achieve very high (97 to 99+%) control and treatment efficiencies and correspondingly low quantities (although not absolutely zero) of discharged constituents.

In areas of the country where very severe and extended cold weather prevails, total recycle of process water become difficult for two reasons:

1. The return water piping and pumping must be protected against freezing. However, technology such as buried

water mains and enclosed, heated pumping stations has been aptly demonstrated in the chemical industry and in water supply operations.

2. The settling ponds may freeze. In a total recycle system, this circumstance would prevent the required water from being supplied back to the process. If auxiliary fresh water supply were provided to uncouple the process from frequent climatic perturbations, the pond system would have to consist of sufficient holding capacity to prevent temporary overflow and would have to contain sufficient evaporative capacity to prevent long-term accumulation of water.

Both of the above difficulties are formidable but not unyielding to practicable, currently available technology. All aspects of manufacturing including waste management assume different stances when the chosen environment is far more severe than the norm; however, currently-available technology can cope with environmental challenges of this sort including the special challenges in waste management.

Recommended Effluent Limitations Guidelines Based Upon Best Practicable Control Technology Currently Available

In view of the existence of three plants (028, 159, and 181) which have already achieved zero discharge of elemental phosphorus; in view of the existence of two plants (TVA and 181) which have already achieved zero discharge of other process waters; in view of the conclusion that "Best Practicable Control Technology Currently Available" is sufficient to achieve zero discharge in other plants (such as Plants 028 and 159); and in full view of the statutory national goal of eliminating the discharge of all pollutants; it is recommended that the best practicable control technology currently available be no discharge of process waste water pollutants to navigable waters.

Waste water from Ore Washing the Beneficiation

The best practicable control technology currently available recommended in the previous paragraphs do not include wastes from the beneficiation or washing of phosphate rock. This beneficiation is commonly but not exclusively conducted at a separate off-site location. The huge raw waste load from benefication, 7.5 kkg of gangue per kkg of phosphorus eventually produced, warrants a separate study and separate effluent guidelines.

The Phosphorus Consuming Subcategory

Phossy Water

Gross discharges of phossy water are presently avoided by pumping displaced phossy water form the plant's phosphorus storage tank back into the emptying rail car which brought the phosphorus, and by transporting this displaced phossy water to the phosphorus producing plant for treatment and/or reuse. Such is the practice at Plants 037 and 192.

Smaller quantities of phossy water discharge may also be eliminated through the use of standard engineering techniques. The phosphorus storage tank level control system may be altered to provide an auxiliary water overflow tank with return of the water to the main tank. The avoidance of elemental phosphorus in plant sewer lines can be implemented by more stringent process and operator controls and procedures and by providing traps downstream of reaction vessels.

In view of the harmful qualities of elemental phosphorus and in view of the available choices from state-of-the-art control techniques, the recommended best practicable control technology currently available for phossy water is no discharge of pollutants.

Phosphoric Acid Manufacture

Exemplary Plant 075 operates without the discharge of any process water. There is no fundamental or practical reason why process water should be discharged at all from any dry-process phosphoric acid plant. Minor leaks and spills may be minimized, collected and treated using control techniques generally available and demonstrated in the industry.

The recommended effluent guideline of no discharge of process waste water pollutants applies generally and with special emphasis upon elemental phosphorus (i.e., phossy water) and upon arsenic residues from the purification of phosphoric acid.

Phosphorus Pentoxide Manufacture

The single raw waste constituent is phosphoric acid from water tail-gas seals. Application of two standard techniques would enable total recycle of this waste water:

1. Reduction in waste water quantites by using dilute caustic or lime slurry as tail gas liquor instead of pure water, increasing the absorptive capacity for P_2O_5.

2. Lime treatment and sedimentation to neutralize and to remove the phosphate, permitting total recycle.

In view of the straightforward application of these two techniques, the recommended best practicable control technology currently available

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effluent guideline is no discharge of process waste water pollutants. Since total recycle is practicable technology, this recommended guideline is not affected by modest inaccuracies in the standard raw waste as estimated in Section V.

Phosphorus Pentasulfide Manufacture

The sole source of process waste water is the scrubber liquor for fumes from casting liquid P_2S_5. One control technique would be the use of inert-atmosphere casting or vacuum casting to completely eliminate the need for scrubbing. As an alternate to this approach, the application of three standard techniques would permit total recycle of scrubber water:

1. Use of dilute caustic or lime slurry instead of pure water would reduce the waste water quantities by increasing the adsorptive capacity for P_2O_5 and SO_2.

2. Partial recycle of scrubber liquor from a sump would reduce the waste water quantity by decoupling the buildup of absorbed acids from the mass-transfer requirements for high scrubber flowrates.

3. Lime treatment and sedimentation to neutralize and to remove phosphate, sulfite and sulfate would permit total recycle.

In view of these different practicable alternates, the recommended best practicable control technology currently available is no discharge of process waste water pollutants to navigable waters. Since total recycle is practicable technology, this recommended guideline is not affected by modest inaccuracies in the standard raw waste load as estimated in Section V.

This guideline also applies to any arsenic-rich residues from the purification of P_2S_5; these solid residues may be disposed of by burial as in Plants 147 and 192.

Phosphorus Trichloride Manufacture

The acid wastes from phosphorus trichloride manufacture arise from the hydrolysis of PCl_3 in scrubber water from the reactor/ still, from product storage tanks, from product transferring operations and from container cleaning. The scrubber water may be collected in a sump and recycled to decrease the wasted quantity of scrubber water (while still maintaining sufficient scrubber flow rates for effective mass transfer) and to increase the concentration of waste constituents.

Lime treatment of the wasted water would neutralize the acids and would precipitate the phosphite and phosphate wastes as calcium salts. Subsequent sedimentation in a mechanically-raked clarifier, with the use of a polymeric flocculant, could effectively remove 85 per cent of the suspended solids as a sludge. This sludge may then be hauled as a slurry for direct landfill, or may be dewatered in sand drying beds or mechanically prior to landfilling. The clarified water may then be discharged, with the following recommended best practicable control technology currently available:

Total Dissolved Solids,	5 kg/kkg (10 lb/ton)
Total Suspended Solids,	0.7 kg/kkg (1.4 lb/ton)
pH	6.0 to 9.0

based upon the raw waste load as determined in Section V:

HCl	3 kg/kkg (6 lb/ton)
H_3PO_3 + H_3PO_4	2.5 kg/kkg (5 lb/ton)

The soluble $CaCl_2$ resulting from lime-neutralization of HCl is 4.5 kg/kkg (9 lb/ton); allowing for some small amount of unprecipitated phosphite and phosphate brings the total dissolved solids to 5 kg/kkg (10 lb/ton). The quantity of precipitated $2\ CaHPO_3.3H_2O$, $Ca_3(PO_4)_2$ or $9\ CaO.3P_2O_5.Ca(OH)_2$ is dependent upon the relative quantities of these compounds, but is no more than 4.5 kg/kkg (9 lb/ton). With a sedimentation efficiency of 85 per cent, the total suspended solids in the effluent should be no more than 0.7 kg/kkg (1.4 lb/ton).

In the case of PCl_3 manufacture, the soluble chlorides are not removed by the applicable "Best Practicable Technology Currently Available", so that the recommended best practicable control technology currently available effluent is not zero discharge. In treating the raw wastes, the total quantity of constituents is not reduced: 5.5 kg/kkg (11 lb/ton) in the raw waste vs. 5.7 kg/kkg (11.4 lb/ton) in the treated effluent. However, the treatment does remove the acidity, substituting for it residual alkalinity.

Zero discharge of arsenic-rich reactor/still residues is recommended, since trichloroethylene treatment (as described in Section VII) may be applied.

Phosphorus Oxychloride Manufacture

The types of raw wastes, the types of applicable control and treatment technologies, and the reason for the best practicable control technology currently available not being zero discharge, are all identically parallel for $POCl_3$ manufacture as they are for PCl_3 manufacture. The difference is one of magnitude. For $POCl_3$ manufacture, the raw waste load as determined in Section V is:

HCl	2 kg/kkg (4 lb/ton)
H_2PO_3 + H_3PO_4	0.5 kg/kkg (1 lb/ton)

Using the same rationale as for PCl_3 manufacture, the recommended Best practicable control technology currently available effluent guidelines are:

Total Dissolved Solids,	3.5 kg/kkg (7 lb/ton)
Total Suspended Solids,	0.15 kg/kkg (0.3 lb/ton)
pH	6.0 to 9.0

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The Phosphate Seqment

Sodium Tripolyphosphate Manufacture

Exemplary Plant 042 has no process wastes. The dust collected from the spray dryer qaseous effluent stream is added to the spray dryer solid product stream. The water used for subsequent scrubbinq of this qas stream from the spray dryer is then recycled to the mix area and is used as process water in the neutralization step. The cooling air used for the product temperinq is vented into the spray-dryer vent line upstream of the scrubbinq operation.

This plant is an excellent example where a combination of inprocess controls such as dry dust collection, water reuse, and return to the process of airborne solids have been utilized to totally avoid any aqueous wastes. Plants 006 and 119 also have no discharqe of porcess waters.

In view of this demonstration, and in view of the qeneral applicability of such techniques throughout the industry, the recommended best practicable control technology currently available is no discharge of process waste water pollutants to naviqable waters.

Animal-Feed Grade Calcium Phosphates

Exemplary Plant 182 has no process wastes. Three separate water cycles are used and there is no effluent from any. The acid defluorination scrubber water is neutralized with lime, the solids are settled by pondinq, and the pond effluent is reused as scrubber water. The scrubber water for collection of airborne solids from the reactor and dryer is recirculated with a bleed-off directly into the reactor as process water. Cooling water is recycled through a cooling tower, with the blowdown used as makeup in the solids scrubbinq system instead of beinq wasted. Softened well water is used for cooling water makeup.

This plant is an excellent example where a combination of inprocess controls (dry dust collection, recycle of scrubber water to minimize waste water quantities, return of process waste streams back to the process, and a systems approach towards water use whereby a blowdown stream from one water cycle becomes a makeup stream for another); in combination with a standard lime-treatment, sedimentation and total recycle scrubber water system; results in the discharqe of no aqueous wastes.

In view of this demonstration, and in view of the qeneral applicability of such techniques throughout the industry, the recommended best practicable control technology currently available is no discharge of process waste water pollutants to naviqable waters.

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Food-Grade Calcium Phosphates

The raw aqueous wastes from the manufacture of food-grade calcium phosphates are from two primary and approximately equal sources: the centrate or filtrate from dewatering of the dicalcium phosphate slurry, and the effluent from wet scrubbers which collect airborne solids from product drying operations. Both of these sources contain suspended, finely divided calcium phosphate solids and phosphoric acid from acid units and from excess acid in the reaction liquid. The total raw waste load (from Section V) is:

Process Water Wasted	4,200 l/kkg (1,000 gal/ton)
Total Suspended Solids (2.4%)	100 kg/kkg (200 lb/ton)
Phosphoric Acid (0.7%)	30 kg/kkg (60 lb/ton)

The first type of currently-available control technology that may be applied is the substitution of dry dust bag collectors for wet scrubbers, as has been done at Plants 003, 042, 119, and 182. The fact that a multi-product plant must provide a separate baghouse for each product does not deny the current availability of this technology but rather increases the cost of such an installation. However, Plant 003, which is a multiple-product, food-grade, calcium phosphates plant, has justified the installation of separate baghouses on the sole basis of profitability from product recovery.

The elimination of wet scrubbing systems would halve the aqueous waste load, so that it would then consist of 2,100 l/kkg (500 gal/ton) containing 2.4 per cent of suspended solids amounting to 50 kg/kkg (100 lb/ton) and containing 0.7 per cent of phosphoric acid amounting to 15 kg/kkg (30 lb/ton).

Standard lime treatment and sedimentation may then be utilized to neutralize these remaining wastes, to precipitate the phosphate, and to remove a nominal 85 per cent of the suspended solids (with the possible aid of a polymeric flocculant). At a pH of 10.5, the remaining concentration of dissolved solids would be approximately 85 per cent of the original quantity, with the remainder landfilled as sludge. The clarified overflow would then consist of 1,800 l/kkg (430 gal/ton) containing:

Dissolved Solids	0.0005 kg/kkg (0.001 lb/ton)
Suspended Solids	11 kg/kkg (22 lb/ton)

In the case for treatment of PCl_3 and $POCl_3$ wastes, previously discussed in this Section, gravity sedimentation after lime treatment was judged adequate for best practicable control technology currently available since the quantity of suspended solids discharged was already much smaller than the quantity of non-removable dissolved solids. In this case for treatment of food-grade calcium phosphate wastes, however, the

reverse is true: the great bulk of the wastes discharged after gravity sedimentation is in the form of suspended solids. Hence, it is judged that more extensive treatment should be sought to approach the national goal of eliminating the discharge of all pollutants.

The demonstrated practice at Plant 006, after lime treatment for neutralization and for precipitation of phosphate wastes, is the direct vacuum filtration of all of the resulting slurry; a practice adopted when gravity sedimentation was judged inadequate by plant personnel. Vacuum filtration (possibly after conditioning with a polymeric flocculant) can reduce the suspended solids content of the waste water from phosphates to the level of 0.5 mg/l. Based upon these data and upon the level of dissolved phosphates of 0.3 mg/l, the discharge would contain (on the basis of the total process water wasted, 4,200 l/kkg (1,000 gal/ton)):

Total Dissolved Solids	0.0015 kg/kkg (0.003 lb/ton)
Total Suspended Solids	0.0025 kg/kkg (0.005 lb/ton)

With the achievement of these extremely low levels of TDS and TSS, or even with considerable relaxation of these levels, the treated-waste water from the manufacture of food-grade calcium phosphates is expected to meet the U.S. Food and Drug Administration criteria for process water and this treated water can then be recycled back into the process. No product purity restrictions exist any longer which had previously necessitated discharge. In fact, once the commitment towards total recycle is made, the lime treatment step may be bypassed since the ionic species from the dissolved solids and the phosphoric acid are precisely those desired in the reaction vessel.

Since the above rationale is entirely based upon demonstrated, currently-available treatment technology, the proposed best practicable control technology currently available is no discharge of process waste water pollutants to navigable waters.

SUMMARY OF PROPOSED BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

No Discharge of Process Waste Water Pollutants

The proposed best practicable control technology currently available for process waste water is no discharge of pollutants for the manufacture of the following chemicals:

Phosphorus Subcategory
- Phosphorus (and Ferrophosphorus)

Phosphorus Consuming Subcategory
- Phosphoric Acid (Dry Process)
- Phosphorus Pentoxide

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Phosphorus Pentasulfide
Phosphate Subcategory
Sodium Tripolyphosphate
Calcium Phosphate (Food-Grade)
Calcium Phosphates (Animal-Feed Grade)

Permitted Discharge

The proposed best practicable control technology currently available for process water for the manufacture of PCl_3 and $POCl_3$ are:

	maximum 30 day average	
	Phosphorus Trichloride	Phosphorus Oxychloride
Total Suspended Solids:*		
kg/kkg	0.7	0.15
lb/ton	1.4	0.3
Total Dissolved Solids:*		
kg/kkg	5	3.5
lb/ton	10	7
pH	6.0-9.0	6.0-9.0

The above guidelines apply to maximum averages of daily values for any period of 30 consecutive days.

The pH range is to be maintained at all times.

* Suspended solids are essentially calcium phosphate and the dissolved solids are calcium chloride.

The permitted maximum concentration for any one day period for suspended and dissolved solids is twice that of the consecutive 30 day average value.

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SECTION X

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE, EFFLUENT GUIDELINES AND LIMITATIONS

INTRODUCTION

The effluent limitations which must be achieved by July 1, 1983 are based on the degree of effluent reduction attainable through the application of the best available technology economically achievable. For the phosphate manufacturing industry, this level of technology was based on the very best control and treatment technology employed by a specific point source within the industrial category or subcategory, or where it is readily transferable from one industry process to another. Best available technology economically achievable places equal emphasis upon in-process controls as upon control or treatment techniques employed at the end of a production process.

Those plant processes and control technologies which at the pilot plant, semi-works, or other level, have demonstrated both technological performances and economic viability at a level sufficient to reasonably justify investing in such facilities were also considered in assessing best available technology economically achievable. This technology is the highest degree of control technology that has been achieved or has been demonstrated to be capable of being designed for plant scale operation up to and including "no discharge" of pollutants. Although economic factors are considered in this development, the costs for this level of control are intended to be for the top-of-the-line of current technology subject to limitations imposed by economic and engineering feasibility. However, best available technology economically achievable may be characterized by some technical risk with respect to performance and with respect to certainty of costs. Therefore, this technology may necessitate some industrially-sponsored development work prior to its application.

The following factors were taken into consideration in determining best available technology economically achievable:

a. The age of equipment and facilities involved;

b. The process employed;

c. The engineering aspects of the application of various types of control techniques;

d. Process changes;

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e. Cost of achieving the effluent reduction resulting from application of best available technology economically achievable and

f. Non-water quality environmental impact (including energy requirements).

PROCESS WATER GUIDELINES

Process water is defined as any water coming into contact with raw materials, intermediates, products, by-products, or gas or liquid that has accumulated such constituents

Based upon the information contained in Sections III through IX of this report, the following determinations were made on the degree of effluent reduction attainable with the application of the best available control technology economically achievable in the various categories of the phosphate manufacturing industry.

All Chemicals Except Phosphorus Trichloride and Phosphorus Oxychloride

The recommended best available technology economically achievable for process water are the same as the best practicable control technology currently available guidelines, i.e., no discharge of process waste water pollutants to navigable waters for the manufacture of the following chemicals:

Phosphours Production Subcategory
- Phosphorus (and Ferrophosphorus)

Phosphorus Consuming Subcategory
- Phosphoric Acid (Dry Process)
- Phosphorus Pentoxide
- Phosphorus Pentasulfide

Phosphate Subcategory
- Sodium Tripolyphosphate
- Calcium Phosphates (Food-Grade)
- Calcium Phosphates (Animal-Feed Grade)

Manufacture of Phosphorus Trichloride and Phosphorus Oxychloride

In-Process Controls

The largest contribution to the raw waste load from these processes is from the escape of PCl_3 vapor from the reactor/stills. The methods for drastically reducing this contribution are clearcut: the substitution of refrigerated condensers for watercooled condensers (or the addition of refrigerated condensers downstream of water-cooled condensers). Refrigerated condensers are already in use at Plant 037 in the manufacture of $POCl_3$ by the air-oxidation process.

As an added step, a demister can be added downstream of the refrigerated condenser to prevent condensed but dispersed PCl_3 from escaping to the scrubber. One concept for this demister is a short section of column packed with metal packing (for good heat transfer) within the refrigerated condenser.

As a corollary to this principle, other sources of PCl_3 and $POCl_3$ vapors could be controlled by refrigerated condensers or cold traps. The storage tank vent and vents for the transfer of liquid product are included in this concept. Alternately, the liquid products could be maintained at low temperatures by refrigerating coils in the storage tanks, so that vapors from storage and transfer would be minimized.

In view of the order-or-magnitude or greater reduction in the vapor pressure of these products resulting from readily-available refrigeration levels, plus the effect on PCl_3 condensation from doubling (or more) the temperature driving force for heat transfer, a reasonable expectation is that the PCl_3 vapor (and mist) losses could be cut to 10 per cent of the present values.

The acid wastes from washing tank cars and tank trucks, and from washing used $POCl_3$ filter elements are very small at present amounting to 0.014 kg/kkg (0.028 lb/ton) of HCl and 0.003 kg/kkg (0.007 lb/ton) of total phosphates. (see table 8) These are very small fractions of the total raw waste load discussed in section V. The wastes from washing returnable nickel drums, however, is estimated to be much larger. Should this raw waste indeed prove significant, the returnable container usage could be abandoned in favor of non-returnable epoxy-lined drums (as is the partial practice at Plant 147 for PCl_3).

Another minor source of wastes is the generation of HCl (not PCl_3) from the reactor/stills, resulting from small quantities of stray moisture in the vessels. The HCl is driven off as a non-condensible while the corresponding H_3PO_3 and H_3PO_4 is retained as reactor residue.

All in all, the above outlined in-process control techniques could drastically reduce the raw waste load to perhaps 10 per cent of the original value, so that the estimated raw waste quantities would then become (for either PCl_3 or $POCl_3$) manufacture):

HCl	0.3 kg/kkg (0.6 lb/ton)
H_3PO_3 + H_3PO_4	0.25 kg/kkg (0.5 lb/ton)

As important as the reduction in the waste water constituent quantities would be a corresponding reduction in the quantity of waste water generated. Tail-gas scrubbers should be very much smaller and should require much lower water flowrates.

As an added step, the scrubber water could be recycled from a sump, thereby decoupling the waste water quantity (blowdown from the sump) from the mass-transfer requirements for scrubbing. Furthermore, water use could be cascaded in the plant, with (for example), the waste water from tank car washing being used as makeup in the tail-gas scrubber system.

End of Process Treatment

At the new low levels of waste water flowrates and constituent quantities, simple lime neutralization of moderate pH (without sedimentation) would result in the following waste water characteristics:

Waste water Quantity	500 l/kkg (120 gal/ton)
Total Dissolved Solids	0.5 kg/kkg (1.0 lb/ton)
Total Suspended Solids	0.35 kg/kkg (0.7 lb/ton)
pH	6-9

Further lime neutralization and removal of suspended solids would not appreciably reduce the quantity of total dissolved solids, and would trade off reduction in total suspended solids for higher pH levels.

At this point, the waste water quantity would be extremely low, and a practicable final step would be evaporation to dryness. An idea of the costs of evaporation can be obtained by assuming a plant manufacturing 59 kkg/day (65 tons/day) of total PCl_3 and $POCl_3$. The waste water quantity would be 30,000 liters/day (7,800 gal/day). Using the data of Section VIII for single-effect evaporation,

Capital Cost =	$6,700	
Annual Costs:	Capital Recovery	= $ 1,600
	Taxes & Insurance	= 300
	Operation & Maintenance (including energy)	= 14,700
		$16,600
Unit Cost = $0.85/kkg ($0.77/ton)		

This unit cost is only 0.3 per cent of the current selling price, $295/kkg ($268/ton).

It is entirely possible that a rigorous economic evaluation might result in a decision to dispose of the original raw waste load by evaporation, rather than to bear the expense of the in-process controls discussed above which minimize (but do not eliminate) the waste. The waste water quantity to be evaporated would be the original quantity, 5,000 l/kkg (1,200 gal/ton), or 300,000 liters/day (78,000 gal/ton); and the costs would be:

Capital Cost = $38,400

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Annual Costs:	Capital Recovery	= 8,900
	Taxes & Insurance	= 1,900
	Operation & Maintenance (including energy)	= 147,000

Unit Cost = $8.10/kkg ($7.35/ton)

Using the most conservative approach, i.e., to evaporate all of the waste water without any in-process control to reduce its quantity, would cost 2.8 per cent of the current selling price. The fundamental reason is that despite the high unit cost of evaporating water, the waste water quantities for PCl_3 and $POCl_3$ are very small. The conclusion is reached that the application of this available technology is economically achievable.

The final step of total evaporation would bring the PCl_3 and $POCl_3$ manufacturing processes into line with the rest of the phosphate industry by achieving the national goal of eliminating the discharge of all pollutants.

It is therefore recommended that the best control technology economically achievable PCl_3 and $POCl_3$ manufacture be no discharge of process waste water pollutants to navigable waters.

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS AND PRETREATMENT RECOMMENDATIONS

INTRODUCTION

This level of technology is to be achieved by new sources. The term "new source" is defined in the Act to mean "any source, the construction of which is commenced after publication of proposed regulations prescribing a standard of performance". New source performance standards are to be evaluated by adding to the consideration underlying the identification of best available technology economically achievable a determination of what higher levels of pollution control are available through the use of improved production processes and/or treatment techniques. Thus, in addition to considering the best in-plant and end-of-process control technology; identified in best available technology economically achievable, new source performance standards are to be based upon an analysis of how the level of effluent may be reduced by changing the production process itself. Alternative processes, operating methods or other alternatives were to be considered. However, the end result of the analysis identifies effluent standards which would reflect levels of control achievable through the use of improved production processes (as well as control technology), rather than prescribing a particular type of process or technology which must be employed. A further determination which was to be made for new source performance standards is whether a standard permitting no discharge of pollutants is practicable.

The following factors were to be considered with respect to production processes which were analyzed in assessing new source performance standards:

a. The type of process employed and process changes;

b. Operating methods;

c. Batch as opposed to continuous operations;

d. Use of alternative raw materials and mixes of raw materials;

e. Use of dry rather than wet processes (including substitution of recoverable solvents for water); and

f. Recovery of pollutants as by-products.

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PROCESS WATER GUIDELINES

Based upon the information contained in Sections III through X of this report, the following determinations were made on the degree of effluent reduction attainable with the application of new source standards for the various categories of the phosphate manufacturing industry.

Since the best practicable control technology currently available guidelines for all of the chemicals considered in this study of the phosphate category were no discharge of process waste water pollutants to navigable waters the recommended new source performance standards are identical to the best available technology economically achievable.

PRETREATMENT RECOMMENDATIONS

In addition to the recommendation of new source performance standards and related effluent limitations covering discharges directly into waterways, the constituents of the effluent discharge from a plant which would interfere with, pass through, or otherwise be incompatible with a well designed and operated publicly owned activated sludge or trickling filter waste water treatment plant were identified. A determination was made of whether the introduction of such pollutants into the treatment plant should be completely prohibited.

Waste water Flowrate

A determination must be made on an individual basis about the impact of a plant's discharge upon the total hydraulic capacity of both the municipal collection system and the municipal wastewater treatment plant. At an extreme, hydraulic overloading will result in overflows or bypasses as the capacities of pumping stations (both in the collection system and the raw waste water pumping stations at the treatment plant) are exceeded. It must be remembered that an overflow of combined industrial/municipal waste water has the same adverse environmental effect as an overflow of raw domestic sewage. At a minimum, hydraulic overloading would result in reduced efficiency of the treatment plant because:

* Primary and secondary clarifiers would be operating at excessive overflow rates
* Secondary treatment units (activated sludge or trickling filter) would be operating at a food deficiency since the waste water from the phosphorus chemicals industry would provide no organic material.
* Trickling filters would become flooded (and so anaerobic).
* Grit chambers would have a high linear velocity resulting in the carry-over of grit and the subsequent adverse effects on equipment.
* The capacity of air blowers for activated sludge second-

ary treatment may be exceeded, resulting in reduced levels of dissolved oxygen.
* The capacity of chlorinators may be exceeded, resulting in insufficient disinfection.
* The critical operating parameters of the activated sludge unit may be compromised.

The domestic waste water flowrate follows a well-known diurnal cycle; if the industrial contribution could be staggered to provide flow equalization, the impact of the added flowrate could be minimized. Conversely, sporatic slug discharges could make periodic overloading more probable.

It is recommended that each source of waste water from the phosphate industry be required to provide an analysis of the impact of its flow contribution upon the hydraulic capacity of the publicly-owned collection and treatment system, should it desire to use the public system. This analysis should include the effects of time-varying flowrate.

Suspended Inorganic Solids

High concentrations of suspended inorganic solids might overload the primary sludge collectors, the primary sludge pumps, the sludge thickener, the sludge dewatering operation, and the sludge disposal system. In addition, since these solids provide no organic food for secondary treatment organisms, they would reduce the active biological-solids fraction (i.e., reduce the mixed liquor volatile suspended solids), thereby reducing the efficiency of secondary treatment.

It is recommended that the maximum concentration of suspended inorganic solids be set at 250 mg/l; equivalent to the maximum concentrations normally found in domestic waste waters.

Acidity

While moderate alkalinity may be tolerated since carbon dioxide produced in secondary treatment by the microbial oxidation of organic material will provide neutralization; free mineral acidity normally cannot be tolerated by the organisms in the secondary treatment biomass. The proteins in these organisms are precipitated and coagulated at pH 4 to 5.

Another strong reason for avoiding acidic contributions to publicly-owned treatment plants is that acidic wastes would drastically promote corrosion of equipment.

It is recommended that the allowable pH range be set at 6 to 10.5.

Dissolved Inorganic Solids

Dissolved inorganic solids would pass through a secondary wastewater treatment plant without being removed. Hence, reliance upon publicly owned treatment plants would be no treatment at all with respect to dissolved solids, and it would be equivalent to direct discharge.

It is recommended that the pretreatment standards for dissolved inorganic solids be the same as the applicable or proposed effluent limitation guidelines.

Heavy Metals or Harmful Materials

Metals or harmful materials would at best, pass through a publicly-owned treatment plant, and at worst, adversely affect the microorganisms in secondary treatment. Elemental phosphorus (as phossy water) and enriched arsenic compounds are potential substances that may be discharged into municipal sewer systems from this industry. Special attention is brought to pretreat wastes for removal of these materials.

It is recommended that the pretreatment standards be no discharge of metals or harmful materials

Dissolved Phosphates

While dissolved phosphates would generally pass through secondary treatment plants with the waste water treatment plant effluent, they would affect the sludge operations. Gravity-thickened sludge (6 to 12 per cent solids) is normally conditioned with lime, ferric chloride, or alum prior to dewatering operations, although polymeric flocculants are also widely used. The phosphates would be precipitated as the calcium, ferric, or aluminum phosphate and would thus render the conditioning step ineffective by partially or totally removing the active cation from solution.

A similar situation exists in tertiary treatment, in the phosphate removal step using lime, ferric chloride, or alum. In this case, the chemical requirements would be increased and the sludge handling capacity of the treatment plant could be overloaded. While these pretreatment standards apply only to secondary plants, precautions should be taken to avoid adverse effects when tertiary treatment might be added in future years.

It is recommended that the maximum permissible phosphate concentration be set at 30 mg/l; equivalent to the maximum concentration normally found in domestic waste waters.

Summary of Recommended Pretreatment

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It is recommended that waste waters discharged from plants in the phosphate manufacturing industry into publicly owned waste water collection and treatment systems conform to the following limitations:

1. An impact analysis of the waste water flowrate (including time-varying effects) upon the hydraulic capacity of the public treatment plant be provided by the phosphorus chemicals plant.

2. The maximum amounts of total dissolved solids be the same as the applicable proposed effluent limitation guidelines.

3. The pH must be between 6 and 10.5.

4. Zero contribution of heavy metals and harmful materials.

5. The maximum concentration of total suspended solids be 250 mg/l.

6. The maximum concentration of total phosphate (as PO_4) be 30 mg/l.

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SECTICN XII

ACKNOWLEDGMENTS

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SECTION XIII

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SECTION XIV

GLOSSARY

All underlined numbers within a chemical formula represent normally subscripted numbers. Physical limitations of the printing device make this system necessary. For Example, H_2O represents water.

Barn

A room-like condensation chamber for anhydrous phosphorus pentoxide.

Burden

The combined rock, coke and silica feed to a phosphorus electric furnace.

Calcination

Heating of a solid to a temperature below its melting point to bring about a state of thermal decomposition or a phase transition other than melting. (73)

DCP

Dicalcium Phosphate Dihydrate, $CaHPO_4 2H_2O$

Dry Process Phosphoric Acid

Phosphoric acid made from elemental phsophorus. Also called furnace acid.

Eutectic

The lowest or highest melting point of an alloy or solution of two or more substances that is comprised of the same components. (73)

Ferrophosphorus

A by-product iron-phosphorus alloy of phosphorus smelting, typically containing 59 percent iron and 22 percent phosphorus. Symbolized as Fe_2P in this report.

Flux

A substance that promotes the fusing of minerals or metals or prevents the formation of oxides. For example, in metal refining lime is added to the furnace charge to absorb mineral impurities in the metal. A slag is formed which floats on the bath and is run off. (73)

Furnace Acid

Phosphoric acid made from elemental phosphorus. Also called dry process phosphoric acid.

Gangue

The minerals and rock mined with a metallic ore but valueless in themselves or used only as a by-product. (73)

Hydrolysis

A chemical reaction in which water reacts with another substance to form one or more new substances. (73)

Immiscible

The property of one liquid being unable to mix or blend uniformly with another.

l

liter

Manufacturing Process

MCP

Monocalcium Phosphate Monohydrate, $Ca(H_2PO_4)_2 - H_2O$

Nodule

Semi-fused agglomerated and calcined phosphate rock particle.

Pdt

Product

Phosphorus Mud

Sludge or emulsion of phosphorus, dust and water.

Phosphorus Oxychloride

$POCl_3$

Phosphorus Pentasulfide

P_2S_5

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Phosphorus Pentoxide

P_2O_5

Phosphorus Trichloride

PCl_3

Phossy Water

Water containing colloidal phosphorus.

Process Water

Any water which, during the manufacturing process, comes into direct contact with any raw material, intermediate, product, by-product, or gas or liquid that has accumulated such consitituents.

Slag

The fused agglomerate which separates in metal smelting and floats on the surface of the molten metal. Formed by combination of flux with ganque of ore, ash of fuel, and perhaps furnace lining. The slag is often the medium by means of which impurities may be separated from metal. (73).

STP

Sodium Tripolyphosphate, $Na_5P_3O_{10}$

TCP

Tricalcium Phosphate, $Ca_3(PO_4)_2$

Transport Water

(1) Water used to carry solids from a site in a slurry form.

(2) Water accompanying a chemical in transport which is either immiscible with water or highly insoluble in water. The water acts acts as a blanket preventing contact of air or other substances with the chemical.

Wet Process Phosphoric Acid

Phosphoric acid made from phosphate rock and sulfuric acid.

TABLE 20

METRIC UNITS

CONVERSION TABLE

MULTIPLY (ENGLISH UNITS)		by	TO OBTAIN (METRIC UNITS)	
ENGLISH UNIT	ABBREVIATION	CONVERSION	ABBREVIATION	METRIC UNIT
acre	ac	0.405	ha	hectares
acre - feet	ac ft	1233.5	cu m	cubic meters
British Thermal Unit	BTU	0.252	kg cal	kilogram - calories
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	F°	0.555(°F-32)*	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	l	liters
gallon/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kw	killowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	lb	0.454	kg	kilograms
million gallons/day	mgd	3,785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square inch (gauge)	psig	(0.06805 psig +1)*	atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
tons (short)	t	0.907	kkg	metric tons (1000 kilograms)
yard	y	0.9144	m	meters

* Actual conversion, not a multiplier

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Subpart A—All Subcategories Except Ducks

§ 412.10 Applicability; description of all subcategories except ducks.

The provisions of this subpart are applicable to discharges resulting from feedlots in the following subcategories: beef cattle—open lots; beef cattle—housed lots; dairy cattle—stall barn (with milk room); dairy—free stall barn (with milking center); dairy—cowyards (with milking center); swine-dirt or pasture lots; swine—housed, slotted floor; swine—solid concrete floor, open or housed lot; sheep—open lots; sheep—housed lots; horses—stables (race tracks); chickens—broilers, housed; chickens—layers (egg production), housed; chickens—layer breeding or replacement stock, housed; turkeys—open lots; turkeys—housed.

§ 412.11 Special definitions.

For the purposes of this subpart:

(a) The term "feedlot" shall mean a concentrated, confined animal or poultry growing operation for meat, milk or egg production, or stabling, in pens or houses wherein the animals or poultry are fed at the place of confinement and crop production is not sustained in the area of confinement.

(b) The term "process waste water" shall mean any water from any source which comes into contact with any manure, litter or bedding, or any other raw material or intermediate or final material or product used in or resulting from the production of animals or poultry or direct products (e.g. milk, eggs).

(c) The term "process waste water pollutants" shall mean pollutants contained in process waste waters.

(d) The term "open lot" shall mean pens or similar confinement areas with dirt, or concrete surfaces wherein animals or poultry are substantially or entirely exposed to the outside environment except for possible small portions affording some protection by windbreaks, small shed-type shade areas. For the purposes hereof the term "open lot" is synonymous with the terms "cowyard" (dairy cattle), "pasture lot" (swine), and "dirt lot" (swine, sheep or turkeys), which are terms widely used in the industry.

(e) The term "housed lot" shall mean totally roofed buildings which may be open or completely enclosed on the sides wherein animals or poultry are housed over solid concrete or dirt floors, slotted (partially open) floors over pits or manure collection areas in pens, stalls or cages, with or without bedding materials and mechanical ventilation. For the purposes hereof, the term "housed lot" is synonymous with the terms "slotted floor" buildings (swine, beef), "barn" or "stable" (dairy cattle, horses), "houses" (turkeys, chickens), which are terms widely used in the industry.

(f) The terms "stall" barn and "free stall" barn shall mean specialized facilities wherein (1) producing cows and replacement cows are milked and fed in a fixed location (stall barn), or (2) producing cows are permitted free movement between resting and feeding areas (free stall barn).

(g) The term "milkroom" shall mean milk storage and cooling rooms normally used for stall barn dairies.

(h) The term "milking center" shall mean a separate milking area with storage and cooling facilities adjacent to a free stall barn or cowyard dairy operation.

§ 412.12 Effluent limitations guidelines representing the degree of effluent reduction obtainable by the application of the best practicable control technology currently available.

(a) The effluent limitation representing the degree of effluent reduction obtainable by the application of the best practicable control technology currently available is no discharge of process waste water pollutants to navigable waters, except for runoff which is not contained by facilities, designed, constructed, and operated to contain all process waste water in addition to the runoff from the 10 year, 24 hour rainfall event as established by the U.S. Weather Bureau for the region in which the point source discharger is located.

(b) Application of the factors listed in section 304(b) does not require variation from the effluent limitation set forth in this section for any point source subject to such effluent limitation.

§ 412.13 Effluent limitations guidelines representing the degree of effluent reduction obtainable by the application of the best available technology economically achievable.

(a) The effluent limitation representing the degree of effluent reduction obtainable by the application of the best available technology economically achievable is no discharge of process waste water pollutants to navigable waters, except for runoff which is not contained by facilities designed, constructed, and operated to contain all process waste water in addition to the 25 year, 24 hour rainfall event as established by the U.S. Weather Bureau for the region in which the point source discharger is located.

(b) Application of the factors listed in section 304(b) does not require variation from the effluent limitation set forth in this section for any point source subject to such effluent limitation.

§ 412.14 Standards of performance for new sources.

(a) The standard of performance representing the degree of effluent reduction obtainable by the application of the best available demonstrated control technology, processes, operating method, or other alternatives is no discharge of process waste water pollutants to navigable waters except for runoff which is not contained by facilities designed, constructed, and operated to contain all process waste water in addition to the runoff from the 25 year, 24 hour rainfall event as established by the U.S. Weather Bureau for the region in which the point source discharger is located.

(b) Application of the factors listed in section 306 does not require variation from the standard of performance set forth in this section for any point source subject to such standard of performance.

§ 412.15 Pretreatment standards for new sources.

The pretreatment standards under section 307(c) of the Act, for a source within the subcategories covered in this subpart which are industrial users of a publicly owned treatment works, (and which would be new sources subject to section 306 of the Act, if it were to discharge pollutants to navigable waters), shall be the standard set forth in Part 128, 40 CFR, except that for the purposes of this section, § 128.133, 40 CFR shall be amended to read as follows: "In addition to the prohibitions set forth in § 128.131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works by a major contributing industry shall be the standard of performance for new source specified in § 412.14, 40 CFR, Part 412, provided that, if the publicly owned treatment works which receives the pollutants is committed, in its NPDES permit, to remove a specified percentage of any incompatible pollutant, the pretreatment standard applicable to users of such treatment works shall be correspondingly reduced for that pollutant."

Subpart B—Ducks Subcategory

§ 412.20 Applicability; description of duck subcategory.

The provisions of this subpart are applicable to discharges from feedlots for the following subcategories:

(a) Ducks—dry lot.

(b) Ducks—wet lot.

§ 412.21 Special definitions.

For the purposes of this subpart:

(a) The term "feedlot" shall mean a concentrated, confined animal or poultry growing operation for meat, milk or egg production, or stabling, in pens or houses wherein the animals or poultry are fed at the place of confinement and crop production is not sustained in the area of confinement.

(b) The term "process waste water" shall mean any water from any source which comes into contact with any manure, litter or bedding, or any other raw material or intermediate or final material or product used in or resulting from the production of animals or poultry or direct products (e.g. milk, eggs).

(c) The term "process waste water pollutants" shall mean pollutants contained in process waste waters.

(d) The term "dry lot" shall mean a totally housed facility for growing ducks in confinement with a dry litter floor cover and expected drinking water use of up to 4.0 gallons of water per duck per day.

(e) The term "wet lot" shall mean a confinement facility for raising ducks which is open to the environment with a small portion of shelter area, and with

open water runs and swimming areas to which ducks have free access with water use in excess of 4.0 gallons per duck per day.

(f) For the purposes of this subpart, the following abbreviations shall have the following meaning: (1) kg shall mean kilogram(s); and (2) lb shall mean pounds.

§ 412.22 Effluent limitations guidelines representing the degree of effluent reduction obtainable by the application of the best practicable control technology currently available.

(a) The effluent limitation representing the degree of effluent reduction obtainable by the application of the best practicable control technology currently available is as follows:

Effluent characteristic	*Effluent Limitation*
BOD5	Maximum for any one day 1.66 kg (3.66 lb) per 1,000 ducks.
	Maximum average of daily values for any period of 30 consecutive days 0.91 kg (2.00 lb) per 1,000 ducks.
Fecal coliform	Maximum at any time 400 counts per 100 ml.

(b) Application of the factors listed in section 304(b) does not require variation from the effluent limitation set forth in this section for any point source subject to such effluent limitation.

§ 412.23 Effluent limitations guidelines representing the degree of effluent reduction obtainable by the application of the best available technology economically achievable.

(a) The effluent limitation representing the degree of effluent reduction obtainable by the application of the best available technology economically achievable is no discharge of process waste water pollutants to navigable waters, except for runoff which is not contained by facilities designed, constructed, and operated to contain all process waste water in addition to the runoff from the 25 year, 24 hour rainfall event as established by the U.S. Weather Bureau for the region in which the point source discharger is located.

(b) Application of the factors listed in section 304(b) does not require variation from the effluent limitation set forth in this section for any point source subject to such effluent limitation.

§ 412.24 Standards of performance for new sources.

(a) The standard of performance representing the degree of effluent reduction obtainable by the application of the best available demonstrated control technology, processes, operating methods, or other alternatives is no discharge of process waste water pollutants to navigable waters, except for runoff which is not contained by facilities designed, constructed, and operated to contain all process waste water in addition to the runoff from the 25 year, 24 hour rainfall event as established by the U.S. Weather Bureau for the region in which the point source discharger is located.

(b) Application of the factors listed in section 306 does not require variation from the standard of performance set forth in this section for any point source subject to such standard of performance.

§ 412.25 Pretreatment standards for new sources.

The pretreatment standards under section 307(c) of the Act, for a source within the subcategories covered in this subpart which are industrial users of a publicly owned treatment works (and which would be new sources subject to section 306 of the Act, if it were to discharge pollutants to navigable waters), shall be the standard set forth in Part 128, 40 CFR, except that for the purposes of this section, § 128.133, 40 CFR shall be amended to read as follows: "In addition to the prohibitions set forth in § 128.131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works by a major contributing industry shall be the standard of performance for new sources specified in § 412.14, 40 CFR, Part 412; provided that, if the publicly owned treatment works which receives the pollutants is committed in its NPDES permit to remove a specified percentage of any incompatible pollutant, the pretreatment standard applicable to users of such treatment works shall be correspondingly reduced for that pollutant."

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[40 CFR Part 422]

PHOSPHATE MANUFACTURING POINT SOURCE CATEGORY

Effluent Limitations Guidelines for Existing Sources and Standards of Performance and Pretreatment Standards for New Sources

Notice is hereby given that effluent limitations guidelines for existing sources and standards of performance and pretreatment standards for new sources set forth in tentative form below are proposed by the Environmental Protection Agency (EPA) for the phosphorus production subcategory (Subpart A), the phosphorus consuming subcategory (Subpart B), and the phosphate subcategory (Subpart C), of the phosphate manufacturing category of point sources pursuant to sections 301, 304(b) and (c), 306(b) and 307(c) of the Federal Water Pollution Control Act, as amended (33 U.S.C. 1251, 1311, 1314 (b) and (c), 1316 (b) and 1317(c); 86 Stat. 816 et seq.; P.L. 92-500) (the "Act").

(a) Legal authority.

(1) *Existing point sources.*—Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which require the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which require the application of best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to section 304(b) to the Act.

Section 304(b) of the Act requires the Administrator to publish regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practible control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operating methods and other alternatives. The regulations proposed herein set forth effluent limitations guidelines, pursuant to section 304(b) of the Act, for the phosphorus production subcategory (Subpart A), the phosphorus consuming subcategory (Subpart B), and the phosphate subcategory (Subpart S), of the phosphate manufacturing category.

(2) *New sources.*—Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants.

Section 306(b)(1)(B) of the Act requires the Administrator to propose regulations establishing Federal standards of performance for categories of new sources included in a list published pursuant to section 306(b)(1)(A) of the Act. The Administrator published in the FEDERAL REGISTER of January 16, 1973 (38 FR 1624) a list of 27 source categories, including the phosphate manufacturing category. The regulations proposed herein set forth the standards of performance applicable to new sources for the phosphorus production subcategory (Subpart A), the phosphorus consuming subcategory (Subpart B), and the phosphate subcategory (Subpart C), of the phosphate manufacturing category.

Section 307(c) of the Act requires the Administrator to promulgate pretreatment standards for new sources at the same time that standards of performance for new sources are promulgated pursuant to section 306. §§ 422.15, 422.25, and 422.35, proposed below, provide pretreatment standards for new sources within the phosphorus production subcategory (Subpart A), the phosphorus consuming subcategory (Subpart B), and the phosphate subcategory. (Subpart

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C), of the phosphate manufacturing category.

Section 304(c) of the Act requires the Administrator to issue to the States and appropriate water pollution control agencies information on the processes, procedures or operating methods which result in the elimination or reduction of the discharge of pollutants to implement standards of performance under section 306 of the Act. The report or Development Document referred to below provides, pursuant to section 304(c) of the Act, information on such processes, procedures or operating methods.

(b) Summary and basis of proposed effluent limitations guidelines for existing sources and standards of performance and pretreatment standards for new sources.

(1) *General methodology.*—The effluent limitations guidelines and standards of performance proposed herein were developed in the following manner. The point source category was first studied for the purpose of determining whether separate limitations and standards are appropriate for different segments within the category. This analysis included a determination of whether differences in raw material used, product produced, manufacturing process employed, age, size, waste water constituents and other factors require development of separate limitations and standards for different segments of the point source category. The raw waste characteristics for each such segment were then identified. This included an analysis of (1) the source, flow and volume of water used in the process employed and the sources of waste and waste waters in the operation; and (2) the constituents of all waste water. The constituents of the waste waters which should be subject to effluent limitations guidelines and standards of performance were identified.

The control and treatment technologies existing within each segment were identified. This included an identification of each distinct control and treatment technology, including both in-plant and end-of-process technologies, which are existent or capable of being designed for each segment. It also included an identification of, in terms of the amount of constituents and the chemical, physical, and biological characteristics of pollutants, the effluent level resulting from the application of each of the technologies. The problems, limitations and reliability of each treatment and control technology were also identified. In addition, the non-water quality environmental impact, such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, noise and radiation were identified. The energy requirements of each control and treatment technology were determined as well as the cost of the application of such technologies.

The information, as outlined above, was then evaluated in order to determine what levels of technology constitute the "best practicable control technology currently available," "best available technology economically achievable" and the "best available demonstrated control technology, processes, operating methods, or other alternatives." In identifying such technologies, various factors were considered. These included the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the process employed, the engineering aspects of the application of various types of control techniques, process changes, non-water quality environmental impact (including energy requirements) and other factors.

The data upon which the above analysis was performed included EPA permit applications, EPA sampling and inspections, consultant reports, and industry submissions.

The pretreatment standards proposed herein are intended to be complementary to the pretreatment standards proposed for existing sources under Part 128 of 40 CFR. The bases for such standards are set forth in the FEDERAL REGISTER of July 19, 1973, 38 FR 19236. The provisions of Part 128 are equally applicable to sources which would constitute "new sources," under section 306 if they were to discharge pollutants directly to navigable waters, except for § 128.133. That section provides a pretreatment standard for "incompatible pollutants" which requires application of the "best practicable control technology currently available," subject to an adjustment for amounts of pollutants removed by the publicly owned treatment works. Since the pretreatment standards proposed herein apply to new sources, §§ 422.15, 422.25 and 422.35 below amend §128.133 to require application of the standard of performance for new sources rather than the "best practicable" standard applicable to existing sources under sections 301 and 304(b) of the Act.

(2) Summary of conclusions with respect to the phosphorus production subcategory (Subpart A), the phosphorus consuming subcategory (Subpart B), and the phosphate subcategory (Subpart C), of the phosphate manufacturing category of point sources.

(i) Categorization.

For the purpose of studying waste treatment and effluent limitations, the phosphate manufacturing category was divided into three discrete subcategories which coincide with a breakdown of the category according to the flow of materials as outlined in the Development Document for the phosphate manufacturing category.

(1) *Subpart A.*—Phosphorus Production Subcategory: Phosphorus (and by-product ferrophosphorus) production stands by itself as a smelting operation, as opposed to more conventional chemical processes. In phosphorus production, a grossly impure raw material is involved, and raw wastes and byproducts are generated which dwarf the quantities of the primary product recovered. The remainder of the industry starts with relatively pure materials, and waste streams are consequently much smaller.

(2) *Subpart B.*—Phosphorus Consuming Subcategory: The chemicals that are made directly from elemental phosphorus (dry process phosphoric acid, phosphorus pentoxide, phosphorus pentasulfide and phosphorus trichloride) may be grouped together because aqueous wastes arise primarily from sources other than the direct process stream. Air pollution abatement unit operations, product purification residues, tail gas seals, vessel cleanings, and leaks and spills are the sources of the aqueous waste streams. Phosphorus oxychloride has been added despite the fact that phosphorus is not a direct raw material of its production; however, the waste streams have similar origins.

(3) *Subpart C.*—Phosphate Subcategory: The chemicals that are made from phosphoric acid include sodium tripolyphosphate and the calcium phosphates. The calcium phosphates include both the animal or livestock feed grade and the human food grade products. These constitute a separate segment because large volumes of process water is used in their manufacture, and also because they are finely divided solid products. The former characteristic gives rise to some aqueous wastes of direct process origin; the latter characteristic gives rise to aqueous wastes from wet dust scrubbing equipment. Most of the animal feed grade phosphate of this subcategory is not made from dry process phosphoric acid produced by industries of Subpart B, the phosphorus consuming subcategory. The livestock feed grade product is mainly produced from wet process phosphoric acid.

(ii) Waste characteristics.

The pollutants contained in raw waste waters resulting from the phosphate manufacturing category include fluoride compounds, arsenic compounds, elemental phosphorus, phosphoric acid, sulfurous acid, sulfuric acid, hydrochloric acid, suspended solids, chromates, total dissolved solids and ammonia. Large volumes of cooling water are required by the industry; heat is a raw waste water problem. Five potentially harmful components were noted in raw waste water streams at objectionable concentrations. These were elemental phosphorus, fluorine compounds, arsenic compounds, free inorganic acids and chromates. Some western ores contain considerable cadmium. This element does not normally appear in the waste water discharges of the phosphate manufacturing category, even when present in the ore at a significant level. Vanadium and radium also occur in some ores and must be considered as potential waste water components.

Noncontact cooling water, process and product water, transport water, contact cooling or heater water, atmospheric seal water, scrubber water, and auxiliary process water form the principal waste water streams in phosphate manufacturing. Raw waste load data have been collected on these streams for each subcategory of the industry, and information assembled on the treatment procedures required for each waste water stream.

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(iii) Origin of waste water pollutants in the phosphate manufacturing category.

(1) Phosphorus production subcategory: An extremely large quantity of non-contact cooling water is employed. Electrostatic precipitators utilized ahead of phosphorus removal sprays collect a dust that contains about 50 percent phosphorus pentoxide with other solids. A sludge originates in the phosphorus condenser sump. This is a mixture of dispersed phosphorus, and other solids that escaped through the stack electrostatic precipitator.

The calciner and furnace fume scrubber liquor waste components are SiO_2, Fe_2O_3, and phosphates, sulfates and fluorides as dissolved solids. The scrubber water is highly acidic from pick-up of sulfur dioxide, and acidic fluorine compounds.

The phosphorus condenser liquor is the main "phossy" water source. Phossy water, a colloidal dispersion of elemental phosphorus, is extremely harmful to aquatic organisms and a major waste water problem. Phossy water occurs from many other sources, whenever elemental phosphorus is handled. Phossy water develops in the water seals and water covers maintained over storage and shipping containers, from washing operations to purify phosphorus, and container cleaning operations.

The slag quenching liquor stream is characterized by suspended solids and dissolved solids, primarily as sulfates. The waste water contains fluorine compounds in the soluble and suspended forms.

(2) Phosphorus Consumption Subcategory: Phossy water is generated whenever elemental phosphorus is stored and shipped. The manufacturing processes are dry, except for use of some water in phosphoric acid production. Waste water pollutants primarily originate from spills, leaks into water seals, and cleanup of equipment and shipping containers.

Water scrubbers, used to pick up fumes from casting of phosphorus pentasulfide, are a source of pollution. Phosphorus trichloride and phosphorus oxychloride manufacture utilize chlorination steps. This leads to the formation of hydrochloric acid. The chlorides do not precipitate in usual treatment operations and constitute a difficult waste water problem.

(3) Phosphate Subcategory: The aqueous wastes from this segment of the industry arise from the use of wet scrubbing equipment, spray and dust deposits, clarified waste water from centrifuges, and filtrate fractions. The pollutants are largely sodium and calcium phosphates, which give rise to suspended and soluble solids in waste water.

A defluorination process utilized in feed grade phosphate production leads to formation of a large suspended solids waste water fraction.

(iv) Treatment and control technology.

In-plant procedures to control pollution include good housekeeping, control of spills, reduction and control of start-up and shut down operations, reuse of waste water, recycle of sediment to raw material supply, salvage of sediment and incorporation in the final product salvage of intermediate products for sale as byproduct, and control of runoff and seepage from lagoons.

"End-of-pipe" waste water treatment processes include sedimentation, flocculation, precipitation, filtration, neutralization, holding basins, lagoons, spray ponds, cooling towers, condensers, disposal of solids to landfill areas, continuous monitoring of cooling water, evaporation and recycle. Treatment technology from this industry requires segregation of process water and cooling water. Process water commonly reused after lime treatment and sedimentation. Phossy water is commonly treated before reuse by holding in a settling pond, neutralization with lime, treatment with a flocculation aid and then additional clarification. Total process waste water recycle is being practiced in segments of the industry.

Air pollution control processes include precipitation, filtration, demisting, stack washing, use of separator towers, cyclone separation, and diversion of components originating in air pollution control processes to waste water treatment systems, to raw materials, and to products. Wet scrubbing of stacks leads to heavy contamination of waste water.

Solid waste control must be considered. The waste water from the phosphate industry, and treatment processes of the industry develop a considerable volume of highly hydrated fluorsilicaceous and silicaceous substance. These hydrated solid wastes form relatively unstable landfill deposits. Best practicable control technology and best available control technology as they are known today, require disposal of the pollutants removed from waste waters in this industry in the form of solid wastes and liquid concentrates. In most cases these are nonhazardous substances requiring only minimal custodial care. However, some constituents may be hazardous and may require special consideration. In order to ensure long term protection of the environment from these hazardous or harmful constituents, special consideration of disposal sites must be made. All landfill sites where such hazardous wastes are disposed, should be selected so as to prevent horizontal and vertical migration of these contaminants to ground or surface waters. In cases where geologic conditions may not reasonably ensure this, adequate legal and mechanical precautions (*e.g.* impervious liners) should be taken to ensure long term protection to the environment from hazardour materials. Where appropriate, the location of solid hazardous materials disposal sites should be permanently recorded in the appropriate office of legal jurisdiction.

(v) Treatment and control technology within subcategories.

Waste water treatment and control technologies have been studied for each subcategory of the industry to determine what is (a) The best practicable control technology currently available, (b) the best available technology economically achievable, and (c) the best available demonstrated control technology, processes, operating methods or other alternatives.

(1) Treatment in phosphorous production subcategory: The best practicable control technology currently available leads to no discharge of the waste components of process waste water from plants of the phosphorus production subcategory. Large amounts of once through cooling water are utilized in the industry. It is vitally important that this be segregated from process waste water. Process waste water can be completely recycled, and reused by lime neutralization and sedimentation. The process waste water is characterized by much suspended phosphorus, silicate, sulfate, fluoride, fluorosilicate and other suspended solids. The treatment system must be protected from excessive intrusion of rain water, and be of adequate volume to handle normal intrusion of peak rainfall periods. The presence of much fine and highly hydrated solids in the waste water typically leads to rapid sealing of most soils. Adverse geologic and hydrologic factors, associated with site selection, may create an environmental uncertainty and could require consideration of adequate impervious liners on the bottoms and sides of treatment ponds to prevent seepage to ground or surface waters.

The requirements for the best available technology economically achievable and for the best available demonstrated control technology, processes, operating methods, or other alternatives for new sources are met by the requirements for the best practicable control technology currently available.

(2) Treatment in the phosphorus consuming subcategory: Best practicable control technology currently available involves segregation of cooling water from process water and treatment and recycle, and reuse of process waste water. Prevention of leaks and spills is important in phosphoric acid production, and for all other products of the subcategory. Total recycle is required for scrubber water in phosphorus pentoxide and phosphorus pentasulfide production. Phosphoric acid is a significant raw waste water contaminant. Lime precipitation is essential in some situations, along with recycle. A special problem is encountered in this subcategory for phosphorus trichloride and phosphorus oxychloride production. The chlorides derived from the chlorination step are not wholly amenable to recycle procedures. A small discharge of total dissolved solids total suspended solids occurs in recycle blowdown. Recycle with lime precipitation and filtration are required operations in phosphorus trichloride and phosphorus oxychloride production.

Condenser coolers are in extensive use in the subcategory. Refrigerated condensers are required for phosphorus trichloride and phosphorus oxychloride production to hold hydrochloric acid

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contamination to a low level. Monitoring is essential to detect and correct process leaks. Contaminated cooling water must be dealt with as process waste water.

Treatment required to achieve best available technology economically achievable, and for best available demonstrated control technology, processes, operating methods or other alternatives for new sources is unchanged from best practical control technology for most products in the subcategory. However, evaporation must be considered to deal with the blowdown from the chlorinated products, phosphorus trichloride and phosphorus oxychloride.

(3) Treatment in the phosphate subcategory: Total recycle, with lime precipitation and dry dust collection, is required in the phosphate subcategory for best practicable control technology currently available. Control of spills and good housekeeping measures are necessary and the segregation of uncontaminated cooling water is essential. Continuous monitoring of condenser cooling water for leaks and provision of emergency storage, and treatment facilities are desirable.

As no discharge of process waste water pollutants to navigable waters is achieved by best practicable control technology currently available, no modifications are required to meet best available technology economically achievable, or best available demonstrated control technology, processes, operating methods, or other alternatives.

(vi) Cost estimates for control of waste water pollutants in the phosphate manufacturing category: Cost estimates follow for processes that can achieve the various levels of treatment required for the three subcategories.

(1) The phosphorus production subcategory: No discharge of process waste water pollutants for the phosphorus production subcategory is achieved through 100 percent recycle of process waste water. No discharge of process waste water pollutants to navigable waters is achieved by 10 percent of the subcategory. Complete recycle would add $4.60/ton of product to the treatment costs of the remaining 90 percent of the subcategory. This 90 percent of the subcategory now applies recycle of phossy water, and recycle of process waste water.

(2) Phosphorus consuming subcategory: No discharge of process waste water pollutants to navigable waters is achieved by 10 percent of the subcategory at an average cost increase of $0.65/ton over the remaining portion of the subcategory. This level of discharge limitation can be achieved by the phosphorus pentoxide segment at a cost of $1.40/ton of product; by the phosphorus pentasulfide segment at a cost of $1.70/ton of product; by the phosphorus trichloride segment using evaporation at a cost of $1.70/ton of product; and, by the phosphorus oxychloride segment using evaporation at a cost of $1.25/ton of product. Best practicable control technology currently available can be achieved by the phosphorus trichloride segment at a cost of $0.70/ton of product and by the phosphorus oxychloride segment at a cost of $0.85/ton of product. All costs are in relation to plants discharging untreated waste waters.

(3) Phosphate subcategory: No discharge of process waste water pollutants to navigable waters is being achieved by all of the sodium tripolyphosphate segment. No additional cost is required to maintain this status. This level of discharge control is achieved in the feed grade dicalcium phosphate segment at a cost of $1.40/ton of product over usual practices, and in the production of food grade dicalcium phosphate at a cost of $1.40/ton of product.

(vii) Establishing daily maximum limitations: The daily maximum limitation of twice the 30 day limitation for total suspended solids and for total dissolved solids in the phosphorus trichloride and phosphorus oxychloride products of the phosphorus consuming subcategory is based on statistical studies of waste generation at existent plants.

(viii) Much consideration has been given to the nonwater quality aspects of pollution control. The large quantities of highly hydrated silicates and fluorosilicates, along with other fine precipitates formed in the treatment processes create a substantial solid waste problem. Landfill and lagoon sites of adequate size and character are essential for treatment processes. The industry produces large quantities of air pollutants. These are separated by a variety of stack treatment processes. Many of the stack wastes create solid waste and waste water problems. The phosphorus production subcategory creates the major air and solids problems.

The soluble chloride salts resultant from evaporation require disposal in a site permanently protected from leaching. These chloride salts remain soluble for an infinite time period. These salts will migrate to ground water, through the inexorable leaching processes normal to soil and normal ground water movement unless extraordinary measures are taken to check the processes.

(ix) Economic impact analysis.

The economic analysis has focused on both internal and external costs associated with the proposed levels of water pollution abatement.

The total investment and annual costs required for all subcategories of this segment of the industry to achieve no discharge of process waste water pollutants to navigable waters by 1977 are estimated at $9.3 million and $4.9 million, respectively. Two segments, phosphorus oxychloride and phosphorus trichloride are not required to achieve this effluent level by 1977, however, the costs to achieve this level of control are included for comparison.

The total cost of water pollution abatement, both operating and raw material costs, for each product has been related to the average product selling price to determine the magnitude of either price increases, if these costs can be passed on, or decreases in pre-tax profitability. These percentages range from 0.6% for phosphorus pentoxide to 1.6 percent for feed-grade dicalcium phosphate.

External cost deals basically with the assessment of economic impact of the internal costs discussed above in terms of price increases, production curtailments or plant closures, resultant employment, community and regional impacts, international trade, and future industry growth. It should be noted that a precise study of economic impact is difficult due to numerous other economic forces at work within an industry, and because of the great variability experienced from plant-to-plant in such factors as pollution control costs, profitability, and return on investment. In an economic study such as this, it is not possible to deal with these factors on an individual plant basis.

It is not expected that any significant economic impact would result from imposing the requirement of no discharge of process waste water pollutants to navigable waters on all covered segments of this category by 1977 (Best Practicable Control Technology for most industry segments). Because of this conclusion, we judge that the proposed guidelines for 1977, 1983 and new sources are economically achievable. The small price increases projected will probably be fully passed on to the consuming industry, since there are few substitutable products. Although the small costs can be passed on by all segments, the sodium tripolyphosphate, and dicalcium phosphate segments would have to absorb costs of any greater magnitude due to declining sodium tripolyphosphate markets and cost-competitive alternates for dicalcium phosphates. In general, the economic viability of no plants in the industry will be threatened by the added burden of the costs. Hence, no production curtailments or plant closures are expected and therefore, there should be no resultant unemployment, community or future growth impacts. because international trading of the products of this industry is of very small significance, and projected price increases are small, the U.S. balance of trade is not expected to be affected by the proposed guidelines.

The report entitled "Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the PHOSPHORUS DERIVED CHEMICALS Segment of the Phosphate Manufacturing Point Source Category" details the analysis undertaken in support of the regulations being proposed herein and is available for inspection in the EPA Information Center, Room 227, West Tower, Waterside Mall, Washington, D.C., at all EPA regional offices, and at State water pollution control offices. A supplementary analysis prepared for EPA of the possible economic effects of the proposed regulations is also available for inspection at these locations. Copies of both of these documents are being sent to persons or institutions affected by the proposed regulations, or who have placed themselves on a mailing list for this purpose (see EPA's Advance Notice of Public Review Procedures, 38 FR 21202, August

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6, 1973). An additional limited number of copies of both reports are available. Persons wishing to obtain a copy may write the EPA Information Center, Environmental Protection Agency, Washington, D.C. 20460, Attention: Mr. Philip B. Wisman.

(c) Summary of public participation. Prior to this publication, the agencies and groups listed below were consulted and given an opportunity to participate in the development of effluent limitations guidelines and standards proposed for the phosphate manufacturing category. All participating agencies have been informed of project developments. An initial draft of the Development Document was sent to all participants and comments were solicited on that report. The following are the principal agencies and groups consulted: (1) Effluent Standards and Water Quality Information Advisory Committee (established under section 515 of the Act); (2) all State and U.S. Territory Pollution Control Agencies; (3) the Fertilizer Institute; (4) Manufacturing Chemists Association; (4) Puerto Rico Land Association; (5) Soap and Detergent Association; (6) The American Society of Mechanic Engineers; (7) Hudson River Sloop Restoration, Inc.; (8) The Conservation Foundation; (9) Environmental Defense Fund, Inc.; (10) Natural Resources Defense Council; (11) The American Society of Civil Defense Council; (12) The American Society of Civil Engineers; (13) Water Pollution Control Federation; (14) National Wildlife Federation, and (15) the Isaac Walton League of America.

The following organizations responded with comments: FMC Corporation, Monsanto Industrial Chemicals Company, State of Pennsylvania, Division of Industrial Wastes and Erosion Control, Delaware River Basin Commission, State of Florida, Department of Pollution Control, United States Department of Interior, Texas Water Quality Board, General Counsel of the Department of Commerce, California Water Resources Control Board, and New York State Department of Environmental Conservation.

The comments were highly variable, ranging from full approval to total rejection.

The primary issues raised in the development of the proposed effluent limitations guidelines and standards of performance and the treatment of these issues herein are as follows:

(1) A common criticism was that few or no plants are actually achieving no discharge of process waste water pollutants to navigable waters in some segments of the industry. As noted in the Development Document, a study of the industry established that this level is being achieved in almost all of these subcategories of phosphate manufacturing. For the remainder, established alternative in-plant and treatment procedures are available for application.

(2) A number of commentators took the position that the pH range, 6.0 to 10.5 originally proposed for process waste water discharges for phosphorus trichloride and phosphorus oxychloride production as the best practicable control technology currently available was too alkaline. The range was changed to pH 6.0 to 9.0.

(3) The criticism was made that lime treatment of phosphate does not eliminate a pollutant but merely substitutes one soluble component for another; actually, lime is highly efficient in removal of many pollutants. Lime treatment of these wastes converts phosphoric acid, and many acidic components from stack washing to insoluble precipitates, without introduction of additional soluble pollutants. Sulfuric acid, sulfurous acid, hydrofluoric acid, and the fluorosilicic acids are removed by lime in remarkably beneficial precipitation reactions.

(4) A number of commenters expressed the opinion that inadequate cost information had been gathered and that these studies were not applied to plants with the full range of treatment problems. The economic impact study, however, has established that cost is not a major factor limiting the attainment of the proposed regulations.

(5) Some comments expressed the opinion that the amount of rainfall at a plant site may be the determining factor in the practicability of meeting regulations requiring no discharge of waste water pollutants. Plants practicing total recycle will have no difficulty in meeting regulations in arid regions. While it may be more difficult to practice total recycle in a humid region than in a dry region, established sound procedures for lagoon design, location, and for control of rainfall run-off are among the factors that make the regulations practicable. It is evident that drainage plans must be optimized for a recycle plant in high rainfall regions. Potential spill and fallout areas requiring control must be limited, as must natural drainage into holding areas. Modified ponds, particularly deeper ponds, can provide extra capacity to carry a plant through periods of unfavorable weather. The regulations covering discharge limitations initiate control operation at dates long into the future. This feature provides manufacturers with the time period required to make the relocation moves, in-plant changes, and waste water treatment changes essential for complying with the Act.

(6) Many comments referred to cooling water, boiler blowdown waste water problems, and water supply waste water problems. These are to be dealt with later as a separate category. Any cooling water that picks up process related pollutants from leaks becomes process waste water. It is the responsibility of the plant to monitor cooling water streams for leaks, and to treat contaminated cooling water to the standards set up for process waste water discharges.

Interested persons may participate in this rulemaking by submitting written comments in triplicate to the EPA Information Center, Environmental Protection Agency, Washington, D.C. 20460, Attention: Mr. Philip B. Wisman. Comments on all aspects of the proposed regulations are solicited. All comments received on or before October 9, 1973, will be considered.

Dated August 31, 1973.

JOHN QUARLES,
Acting Administrator.

PART 422—EFFLUENT LIMITATIONS GUIDELINES FOR EXISTING SOURCES AND STANDARDS OF PERFORMANCE AND PRETREATMENT STANDARDS FOR NEW SOURCES FOR THE PHOSPHATE MANUFACTURING POINT SOURCE CATEGORY

Subpart A—Phosphorus Production Subcategory

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422.10 Applicability; description of phosphorus production subcategory.
422.11 Specialized definitions.
422.12 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.
422.13 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.
422.14 Standards of performance for new sources.
422.15 Pretreatment standards for new sources.

Subpart B—Phosphorus Consuming Subcategory

422.20 Applicability; description of phosphorus consuming subcategory.
422.21 Specialized definitions.
422.22 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.
422.23 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.
422.24 Standards of performance for new sources.
422.25 Pretreatment standards for new sources.

Subpart C—Phosphate Subcategory

422.30 Applicability; description of phosphate subcategory.
422.31 Specialized definitions.
422.32 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.
422.33 Effluent limitations guidelines representing the degree of effluent reduction attainable by application of the best available technology economically achievable.
422.34 Standards of performance for new sources.
422.35 Pretreatment standards for new sources.

Subpart A—Phosphorus Production Subcategory

§ 422.10 Applicability; description of phosphorus production subcategory.

The provisions of this subpart are applicable to the discharges resulting from the production of phosphorus and ferrophosphorus by smelting of phosphate ore.

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§ 422.11 Specialized definitions.

For the purpose of this subpart: the term "process waste water" shall mean any water which, during the manufacturing process, comes into direct contact with any raw material, intermediate product, by-product or product used in or resulting from the manufacture of phosphorus and ferrophosphorus.

§ 422.12 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by a point source subject to the provisions of this subpart: There shall be no discharge of process waste water pollutants to navigable waters.

§ 422.13 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best available technology economically achievable by a point source subject to the provisions of this subpart: There shall be no discharge of process waste water pollutants to navigable waters.

§ 422.14 Standards of performance for new sources.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged reflecting the greatest degree of effluent reduction achievable through application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants by a new point source subject to the provisions of this subpart: There shall be no discharge of process waste water pollutants to navigable waters.

§ 422.15 Pretreatment standards for new sources.

The pretreatment standards under section 307(c) of the Act, for a source within the phosphorus production subcategory, which is an industrial user of a publicly owned treatment works (and which would be a new source subject to section 306 of the Act, if it were to discharge pollutants to navigable waters), shall be the standard set forth in Part 128, 40 CFR, except that for the purposes of this section, § 128.133, 40 CFR, shall be amended to read as follows: "In addition to the prohibitions set forth in § 128.131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works by a major contributing industry shall be the standard of performance for new sources specified in § 422.14, 40 CFR, Part 422 provided that, if the publicly owned treatment works which receives the pollutants is committed, in its NPDES permit, to remove a specified percentage of any incompatible pollutant, the pretreatment standard applicable to users of such treatment works shall be correspondingly reduced for that pollutant."

Subpart B—Phosphorus Consuming Subcategory

§ 422.20 Applicability; description of phosphorus consuming subcategory.

The provisions of this subpart are applicable to discharges resulting from the manufacture of phosphoric acid, phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride directly from elemental phosphorus. The production of phosphorus trichloride and phosphorus oxychloride create waste water pollutants not completely amenable to the procedures utilized for best practicable control technology currently available. The standards set for phosphorus trichloride manufacture and phosphorus oxychloride manufacture, accordingly, must differ from the rest of the subcategory at this level of treatment.

§ 422.21 Specialized definitions.

For the purpose of this subpart:

(a) the term "process waste water" shall mean any water which, during the manufacturing process, comes into direct contact with any raw material, intermediate product, by-product or product used in or resulting from the manufacture of phosphorus and ferrophosphorus.

(b) the term "TSS" shall mean total suspended nonfilterable solids.

(c) the term "TDS" shall mean total dissolved solids. The analytical value for this pollutant is the quantitative difference between the total solids and the total suspended nonfilterable solids.

(d) the term "kg/kkg" shall mean kilograms per 1,000 kilograms.

§ 422.22 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of best practicable control technology currently available by a point source subject to these provisions of this subpart:

(a) There shall be no discharge of process waste water pollutants to navigable water from the manufacture of phosphoric acid, phosphorus pentoxide, or phosphorus pentasulfide.

(b) The following limitations constitute the maximum permissible discharge for phosphorus trichloride manufacturing on the basis of productions:

Effluent characteristic	*Effluent limitation*
TSS	Maximum for any one day 1.4 kg/kkg of product (1.4 lb/1,000 lb). Maximum average of daily values for any period of thirty consecutive days 0.7 kg/kkg of product (0.7 lb/1,000 lb).
TDS	Maximum for any one day 10.0 kg/kkg of product (10.0 lb/1,000 lb). Maximum average of daily values for any period of thirty consecutive days 5.0 kg/kkg of product (5.0 lb/1,000 lb).
pH	6.0 to 9.0.

(c) The following table sets forth the maximum permissible discharge for phosphorus oxychloride on the basis of production:

Effluent characteristic	*Effluent limitation*
TSS	Maximum for any one day 0.3 kg/kkg of product (0.3 lb/1,000 lb). Maximum average of daily values for any period of thirty consecutive days 0.15 kg/kkg of product (0.15 1,000 lb).
TDS	Maximum for any one day 7.0 kg/kkg of product (7.0 lb/1,000 lb). Maximum average of daily values for any period of thirty consecutive days 3.5 kg/kkg of product (3.5 lb/1,000 lb).
pH	6.0 to 9.0.

§ 422.23 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best available technology economically achievable.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best available technology economically achievable by a point source subject to the provisions of this subpart: there shall be no discharge of process waste water pollutants to navigable waters resulting from the manufacture of phosphoric acid, phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride or phosphorus oxychloride.

§ 422.24 Standards of performance for new sources.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged reflecting the greatest degree of effluent reduction achievable through ap-

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plication of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants by a new point source subject to the provisions of this subpart: there shall be no discharge of process waste water pollutants to navigable waters.

§ 422.25 Pretreatment standards for new sources.

The pretreatment standards under section 307(c) of the Act, for a source within the phosphorus consuming subcategory which is an industrial user of a publicly owned treatment works (and which would be a new source subject to section 306 of the Act, if it were to discharge pollutants to navigable waters), shall be the standard set forth in Part 128, 40 CFR, except that for the purposes of this section, § 128.133, 40 CFR shall be amended to read as follows: "In addition to the prohibitions set forth in § 128.131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works by a major contributing industry shall be the standard of performance for new sources specified in § 422.24, 40 CFR, Part 422; provided that, if the publicly owned treatment works which receives the pollutants is committed, in its NPDES permit, to remove a specified percentage of any incompatible pollutant, the pretreatment standard applicable to users of such treatment works shall be correspondingly reduced for that pollutant."

Subpart C—Phosphate Subcategory

§ 422.30 Applicability; description of phosphate subcategory.

The provisions of this subpart are applicable to discharges resulting from the manufacture of sodium tripolyphosphate and calcium phosphates from phosphoric acid.

§ 422.31 Specialized definitions.

For the purpose of this subpart: the term "process waste water" shall mean any water which, during the manufacturing process, comes into direct contact with any raw material, intermediate product, by-product or product used in or resulting from the manufacture of phosphorus and ferrophosphorus.

§ 422.32 Effluent limitations guidelines representing the degree of effluent reduction attainable by the application of the best practicable control technology currently available.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best practicable control technology currently available by a point source subject to the provisions of this Subpart: there shall be no discharge of process waste water pollutants to navigable waters.

§ 422.33 Effluent limitations guidelines representing the degree of effluent reduction attainable by application of the best available technology economically achievable.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged after application of the best available technology economically achievable by a point source subject to the provisions of this Subpart: there shall be no discharge of process waste water pollutants to navigable waters.

§ 422.34 Standards of performance for new sources.

The following limitations constitute the quantity or quality of pollutants or pollutant properties which may be discharged reflecting the greatest degree of effluent reduction achievable through application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants by a new point source subject to the provisions of this Subpart: there shall be no discharge of process waste water pollutants to navigable waters.

§ 422.35 Pretreatment standards for new sources.

The pretreatment standards under section 307(c) of the Act, for a source within the phosphate manufacturing category phosphorus consuming subcategory which is an industrial user of a publicly owned treatment works (and which would be a new source subject to section 306 of the Act, if it were to discharge pollutants to navigable waters), shall be the standard set forth in Part 128, 40 CFR, except that for the purpose of this section, § 128.133, 40 CFR shall be amended to read as follows: "In addition to the prohibitions set forth in § 128.131, the pretreatment standard for incompatible pollutants introduced into a publicly owned treatment works by a major contributing industry shall be the standard of performance for new sources specified in § 422.34, 40 CFR, Part 422; provided that, if the publicly owned treatment works which receives the pollutants is committed, in its NPDES permit, to remove a specified percentage of any incompatible pollutant, the pretreatment standard applicable to users of such treatment works shall be correspondingly reduced for that pollutant."

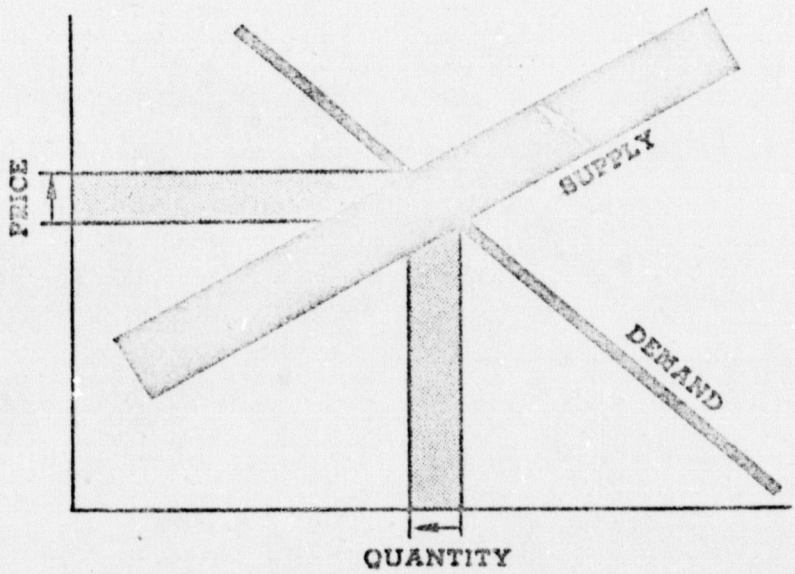
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AUGUST 1973

ECONOMIC ANALYSIS OF PROPOSED EFFLUENT GUIDELINES

THE INDUSTRIAL PHOSPHATE INDUSTRY



U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Planning and Evaluation
Washington, D.C. 20460

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This document is available in limited quantities through the U. S. Environmental Protection Agency, Information Center, Room W-327 Waterside Mall, Washington, D. C. 20460.

The document will subsequently be available through the National Technical Information Service, Springfield, Virginia 22151.

ECONOMIC ANALYSIS
OF
PROPOSED EFFLUENT GUIDELINES

THE INDUSTRIAL PHOSPHATE INDUSTRY

August 1973

EPA-230/1-73-021

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PREFACE

The attached document is a contractors' study prepared for the Office of Planning and Evaluation of the Environmental Protection Agency ("EPA"). The purpose of the study is to analyze the economic impact which could result from the application of alternative effluent limitation guidelines and standards of performance to be established under sections 304(b) and 306 of the Federal Water Pollution Control Act, as amended.

The study supplements the technical study ("EPA Development Document") supporting the issuance of proposed regulations under sections 304(b) and 306. The Development Document surveys existing and potential waste treatment control methods and technology within particular industrial source categories and supports promulgation of certain effluent limitation guidelines and standards of performance based upon an analysis of the feasibility of these guidelines and standards in accordance with the requirements of sections 304(b) and 306 of the Act. Presented in the Development Document are the investment and operating costs associated with various alternative control and treatment technologies. The attached document supplements this analysis by estimating the broader economic effects which might result from the required application of various control methods and technologies. This study investigates the effect of alternative approaches in terms of produce price increases, effects upon employment and the continued viability of affected plants, effects upon foreign trade and other competitive effects.

The study has been prepared with the supervision and review of the Office of Planning and Evaluation of EPA. This report was submitted in fulfillment of Task Order No. 7, Contract 68-01-1541 by Arthur D. Little, Inc. Work was completed as of August 1973.

This report is being released and circulated at approximately the same time as publication in the Federal Register of a notice of proposed rule making under sections 304(b) and 306 of the Act for the subject point source category. The study has not been reviewed by EPA and is not an official EPA publication. The study will be considered along with the information contained in the Development Document and any comments received by EPA on either document before or during proposed rule making proceedings necessary to establish final regulations. Prior to final promulgation of regulations, the accompanying study shall have standing in any EPA proceeding or court proceeding only to the extent that it represents the views of the contractor who studied the subject industry. It cannot be cited, referenced, or represented in any respect in any such proceeding as a statement of EPA's views regarding the subject industry.

This report has been reviewed by the Office of Planning and Evaluation, EPA, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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CERTIFICATE OF SERVICE

I hereby certify that on this 20th day of December, 1974, one copy of the Deferred Joint Appendix to the briefs in the above-captioned cases was served on counsel for Respondent by placing same in the United States mail, first class, postage prepaid, properly addressed to John J. Zimmerman, Attorney, Department of Justice, Washington, D.C.

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